CARBENE-CARBENE REARRANGEMENTS: A STUDY IN THE BENZOCYCLOHEPTATRIENYLIDENE-NAPHTHYLCARBENE SYSTEM

By

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DEDICATION

This dissertation is dedicated to the author's wife, Sherry Lee, whose work, understanding, and love made this work possible and to his daughter, Laura, who provided him with much happiness.

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Major Department: Chemistry

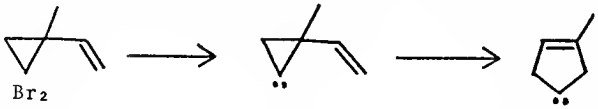
The rearrangement of benzocycloheptatrienylidenes to naphthylcarbenes in solution thermally at temperatures in the range of 100° and photolytically at temperatures as low as -35° is reported. The rearranged naphthylcarbenes were detected by their reaction products with solvent. Decomposition in benzene gave the corresponding naphthylcycloheptatrienes in good yield, and decompositions in cyclohexane and diglyme yielded the corresponding insertion products. In cyclohexene, the formation of naphthylnorcaranes and naphthylcarbene insertion products into cyclohexene was temperature and concentration dependent. This is consistent with a bimolecular reaction of an intermediate with cyclohexene in competition with a unimolecular rearrangement that gives β-naphthylcarbene.

The rearrangement of a carbene precursor was excluded and possible mechanisms were explored. Stereochemical studies indicate that the singlet state of the carbene is responsible for the rearrangement and that there is a small amount of nonstereospecific addition which is unaffected by dilution but is affected by the addition of triplet scavengers. This is compatible with a singlet-triplet equilibrium wherein the rate of triplet-singlet intersystem crossing is greater than the rates of addition of the triplet carbene to olefin, but the rate of triplet carbene addition to dienes (and oxygen) must be greater than the rate of triplet-singlet intersystem crossing. Methyl substitution has an effect upon the rearrangement which may occur via a fused, twisted cyclopropene intermediate (benzobicycloheptatriene) from the boat conformation of the carbene, the planar conformation, or via a concerted pathway.

CHAPTER I

INTRODUCTION AND BACKGROUND

Carbene-carbene rearrangement has been established as a firm, although relatively rare, chapter in the chemistry of divalent intermediates. In 1967, Skattebol[1] reported several examples of "non-trivial" carbene-carbene rearrangements, e.g., that of vinylcyclopropylidene (1) to cyclopentenylidene (2).



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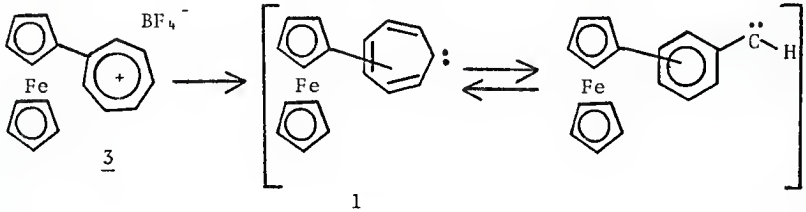
In this type of rearrangement, however, the carbene carbon retains its integrity and, since the carbene was generated by α-elimination, a free carbene may not have been obtained. In fact, the stereoselectivity in product formation in one case suggested a carbenoid species.

Cais et al.[2] reported a carbene-carbene rearrangement in the deprotonation of ferrocenyltropylium fluoborate (3) with the admonition that the carbene intermediacy was not established.



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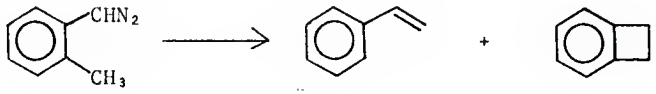
Along a slightly different line, Strausz[3] and coworkers investigated the rearrangement of the carbonylcarbene derived from the photolysis of 3-diazobutanone-2 and homologous compounds in both the gas and condensed phases. Russell and Rowland[4] also investigated similar systems but came to slightly different conclusions.

In 1965, Shechter and Vander Stouw[5] reported the rearrangement of various methyl- and dimethylphenylcarbenes and elucidated this work in a more recent report.[6] In their work, (2-methylphenyl)diazomethane (4), for example, was pyrolyzed to yield, among other products, styrene (5), and benzocyclo-



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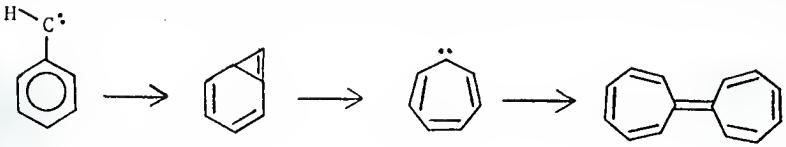
butene (6). The above products and a labeling study indicated the process was occurring via a multiple carbene-carbene rearrangement.

Jones et al.[7] later elaborated on the phenylcarbene-cycloheptatrienylidene rearrangement when heptafulvalene (7) was isolated from the gas phase pyrolysis at 250° of the sodium salt of benzaldehyde tosylhydrazone as well as from pyrolysis of the sodium salt of tropone tosylhydrazone.[8] Pyrolysis of



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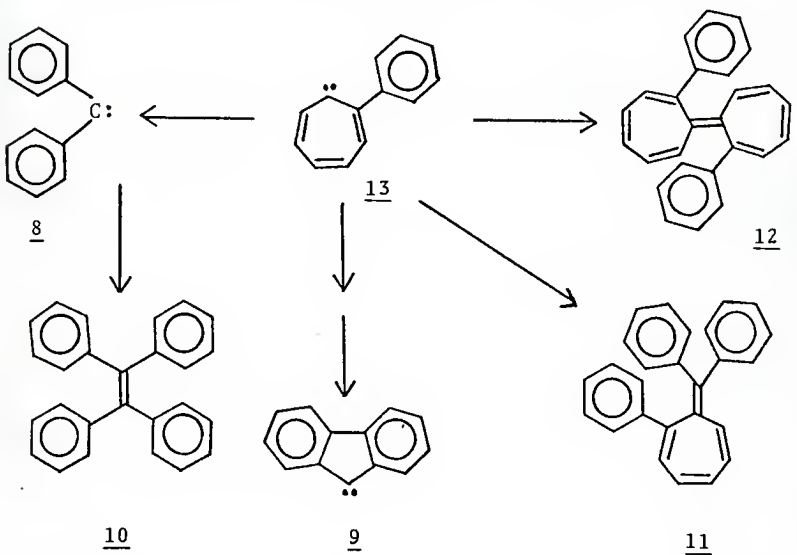
a mixture of the sodium salts of benzaldehyde tosylhydrazone and p-tolualdehyde tosylhydrazone resulted in the formation of crossed dimer which proved that the rearrangement occurred in the gas phase.

Multiple carbene-carbene rearrangements of diphenylmethylene (8) were also studied by Jones.[9] Pyrolysis at 350° of diphenyldiazomethane yielded fluorene (9), tetraphenylethylene (10), triphenylheptafulvene (11), diphenylheptafulvalene (12), and the corresponding azine. Note that these

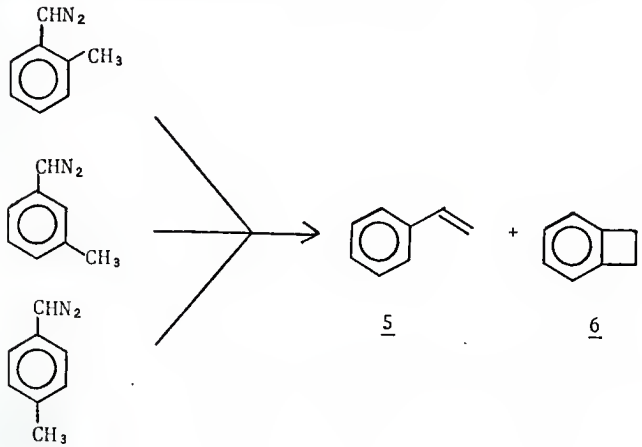


results require that the diarylcarbene expand to form the arylcycloheptatrienylidene 13 and the arylcycloheptatrienylidene contract to form a biphenylmethylene which is the immediate precursor of the fluorene.

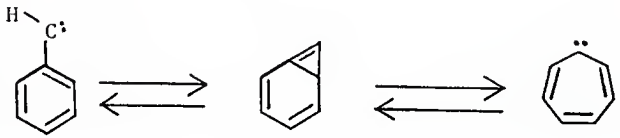
Wentrup and Wilczek[10] also reported the reversibility of the phenylcarbene-cycloheptatrienylidene rearrangement when they isolated stilbene and heptafulvalene from the independent gas phase pyrolysis at 300° of the sodium salts of both benzaldehyde tosylhydrazone and tropone tosylhydrazone.

Hedaya and coworkers[11] studied the ring contraction and expansion of phenylcarbene in the gas phase by pyrolysis of benzaldehyde tosylhydrazone sodium salt. They also observed the formation of heptafulvalene as one of the reaction products and by incorporating a labeling study on tolylcarbene[12] they decided that very small energy barriers separate phenylcarbene, cycloheptatrienylidene, and possible bicycloheptatriene intermediates.

Lastly, M. Jones, Jr.[13] investigated the interconversion of o-, m-, and p-tolylcarbene by observing the ratios of the styrene (5) and benzocyclobutene (6) produced in the pyrolysis of the corresponding diazo compounds.



It is very interesting to note that most of the researchers on the phenylcarbene-cycloheptatrienylidene interconversion believe that the rearrangement occurs via a bicycloheptatriene intermediate (14).[5-7,9-13] Jones and



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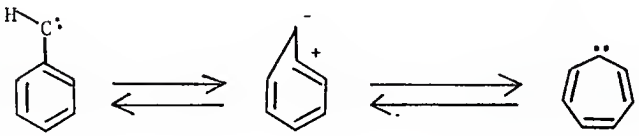
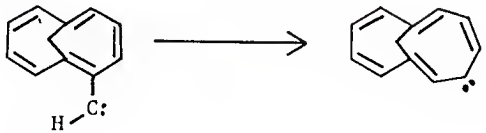
Mitsuhashi[14] elucidated this mechanism with their study on the importance of bond order in the gas phase carbene-carbene rearrangement of a series of substituted naphthylcarbenes. It was found that scrambling of the carbene occurs only between positions having the highest bond order which augurs well for the bicyclic intermediate as opposed to a Wolff-type rearrangement (shown below).



To date, the latest work in carbocyclic carbene-carbene rearrangements was done by Jones and Gebert[15] on the ring expansion of the ten π-electron 1,6-methano[10]annulenyl-2-carbene (15). The products of the reaction are apparently

rearranged dimers and the mechanism is assumed to be similar to that mentioned above.



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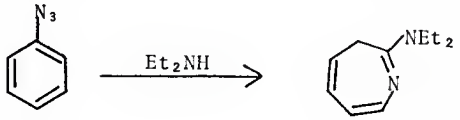
Nitrogen analogues to the phenylcarbene-cycloheptatrienylidene rearrangement have been known for a long time. The ring expansion of phenylnitrene to yield substituted azepines was studied as early as 1958[16,17] and has recently received thorough investigation.[18-24] Pyrolysis[16] and photolysis[24] of phenyl azide (16) in the presence of amines led to 2-amino-3H-azepine derivatives (17) as final products.



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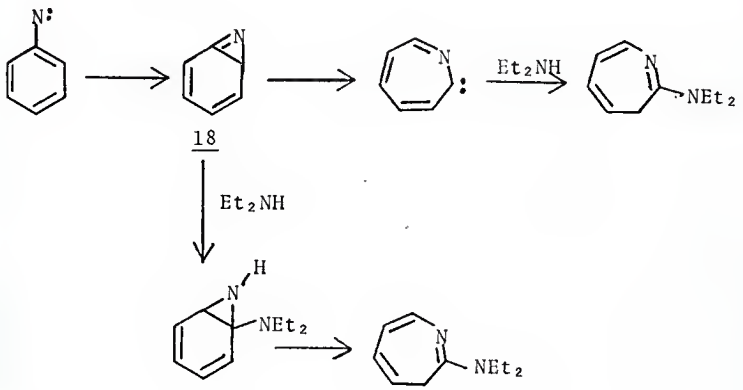
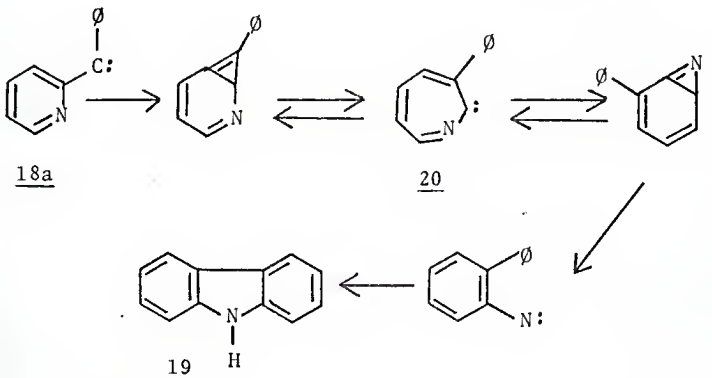
The thermal[19] and photolytic[21,22] deoxygenation of nitrobenzene, as well as the thermal deoxygenation of nitrosobenzene,[18] in the presence of amines also led to 2-amino-3H-azepines. As in the analogous carbene-carbene rearrangements, these reactions can be envisioned as proceeding through a bicyclic intermediate which can yield an azacycloheptatrienylidene. From the experimental results, however, workers have not been able to determine whether or not the azacyclohepta-

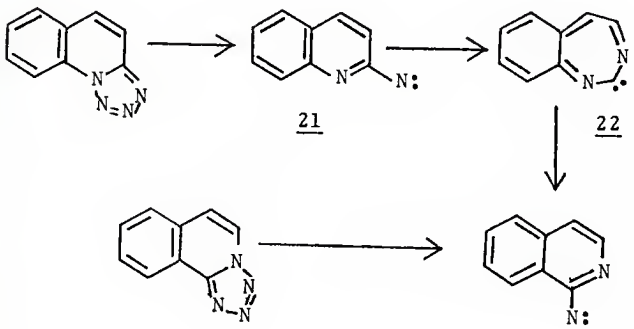
trienylidene is an intermediate. In fact, another mechanism, addition of the amine to the bicyclic azirine (18), has received much more attention.[25]



Crow and Wentrup[26] reported that the thermal generation of 2-pyridylphenylcarbene (18a) led to carbazole (19) products which were believed to arise via a substituted azacyclohepta-



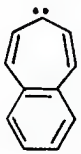
trienylidene (20) intermediate or transition state. Crow and Wentrup have extended their work on these systems[27] as well as investigated the pyridylnitrene-diazacycloheptatrienylidene rearrangement.[28] Perhaps the most interesting was the work on 2-quinolylnitrene (21), an annelated nitrene which is



believed to rearrange via an annelated diazacycloheptatrienylidene (22).[29] However, naphthyl azides have not been known to give rise to detectable azepine.[30]

The work described in this dissertation was done to investigate the effects of annelation on the phenylcarbene-cycloheptatrienylidene rearrangement. It was hoped that the effects of annelation would give insight on the nucleophilicity of the aromatic carbene, on the relative rate of rearrangement and on the mechanism of the rearrangement. The approach was very feasible in that the precursors for both the annelated arylcarbene and the annelated aromatic carbenes were avail-

able. The systems chosen for study were 4,5-benzocyclohepta-trienylidene (23), 2-methyl-4,5-benzocycloheptatrienylidene (24), 2,3-benzocycloheptatrienylidene (25), and the related



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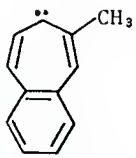

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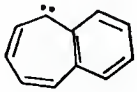

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naphthylcarbenes. While other benzocycloheptatrienylidenes have been prepared and studied, they did not rearrange and many of their reactions were typical of diarylcarbenes.[31]

CHAPTER II

RESULTS

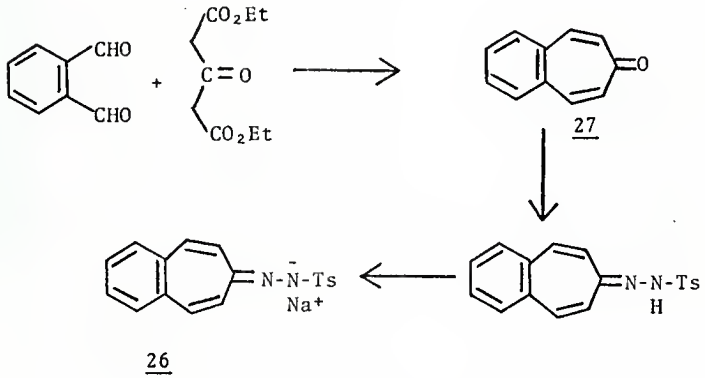
The first results needed were for the model system of phenylcarbene and cycloheptatrienylidene. Thus, the pyrolysis of the sodium salt of benzaldehyde tosylhydrazone was effected in diglyme at 165° to produce what is believed to be the phenylcarbene-diglyme insertion products. This residue, a light yellow oil, had an nmr spectrum very similar to that of the naphthylcarbene-diglyme insertion products (vide infra); there was also benzaldazine produced in the reaction. The nmr spectrum of the reaction material indicated no heptafulvalene was present, and comparative tlc of the material and a known sample of heptafulvalene was carried out using silica gel eluting with pentane. This confirmed the absence of heptafulvalene in the reaction material.

Tropone tosylhydrazone sodium salt was also decomposed in diglyme at a temperature of 210°. The nmr spectrum of the residue, a dark solid, was identical to that of heptafulvalene with an additional small amount of aromatic resonance at 2.8 τ but none at 6.2-7.0 τ (the position expected for the resonances of any diglyme insertion products).

The aromatic carbene, 4,5-benzocycloheptatrienylidene (23), was generated by the thermal and photolytic decomposi-

tion of the sodium salt of 4,5-benzotropone tosylhydrazone (26) in an appropriate solvent. Pyrolysis or photolysis of the sodium salts of tosylhydrazones form the corresponding diazo compounds in situ.[32] The diazo compounds then decompose under aprotic reaction conditions to yield the carbenes.

The synthetic route to the sodium salt of 4,5-benzotropone tosylhydrazone is shown in the scheme below. The



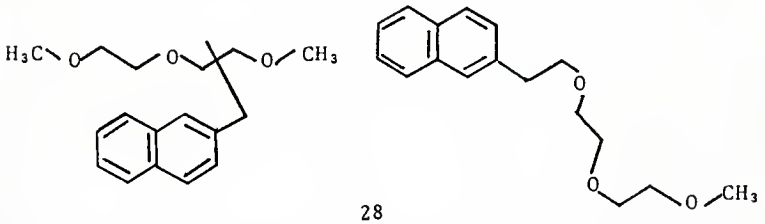
ketone, 4,5-benzotropone (27), was prepared by the method of Thiele and Weitz[33] and the tosylhydrazone by a modification of the procedure of Closs.[34] The conversion of the tosylhydrazone to its sodium salt was done with sodium hydride in tetrahydrofuran.[35] The last step was carried out in a dry box; however, contrary to some reports the sodium salts did not appear to be hygroscopic in most cases.

In a similar manner, commercially available β-naphthaldehyde was converted to its tosylhydrazone[36] and then to its

tosylhydrazone sodium salt. This salt was the immediate precursor of β-naphthylcarbene.

In most cases, the naphthaldehyde tosylhydrazone sodium salt was decomposed under the same or very similar conditions as those of the 4,5-benzotropone tosylhydrazone sodium salt so that the chemistry of the two carbenes could be compared and, where possible, as a check on the authenticity of the naphthyl products formed from the rearranged carbene.

Thus 4,5-benzotropone tosylhydrazone sodium salt was decomposed in diglyme at 100° to give a 29% yield of the isomeric β-naphthylcarbene-diglyme insertion products (28).



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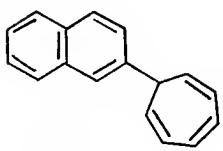
While these isomeric compounds could not be readily separated, there is little doubt as to their identity. The nmr spectrum of these products shows aromatic proton absorptions at 2.00-2.80 τ and methyl and methylene protons adjacent to oxygen at 6.10-7.20 τ (there are more signals than necessary in the region of 6.60 τ for methyl protons of a single product). Other spectral properties and the elemental analysis of the mixture are in complete agreement with the assigned structures, and regardless of the carbene precursor (vide infra), the products formed in diglyme are the same.

The decomposition of naphthaldehyde tosylhydrazone sodium salt in diglyme at 100° produced a 13% yield of the same β-naphthylcarbene-diglyme insertion products produced in the above decomposition. The product yield from the decomposition of the naphthaldehyde tosylhydrazone salt was typically lower because there was competition of aldazine formation.

Next, the photolytic decomposition of the salt of 4,5-benzotropone tosylhydrazone in diglyme was carried out at 30° and resulted in the formation of the familiar naphthylcarbene-diglyme insertion products.

When 4,5-benzotropone tosylhydrazone sodium salt was heated in benzene at 80° there was formed, in 96% yield, a product identified as 2-(2,4,6-cycloheptatrien-1-yl)naphthalene (29). Although this compound has been prepared before, there



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is no complete report of its physical and spectral properties.[37] The existence of the cycloheptatrienyl moiety was proven by comparison of the above compound's nmr spectrum with that of 1-phenyl-2,4,6-cycloheptatriene[38] (the spectra were identical except for the aromatic region). That it was the β-naphthyl function (as opposed to α-naphthyl) was shown by careful

examination of the compound's ir spectrum; the absorption for the out-of-plane bending at 861 cm^{-1} indicated an isolated H on the naphthyl ring system, that at 821 cm^{-1} indicated two adjacent H, and that at 745 cm^{-1} was indicative of four adjacent H[39] (the nmr of the product showed a ratio of 4:3 for the α to β protons, respectively, in the aromatic region). Photolysis at 30° of the sodium salt of 4,5-benzotropone tosylhydrazone also produced the adduct 29 in 59% yield.

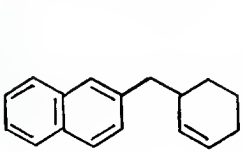
Photolysis (30°) and thermolysis (125°) of the sodium salt of β-naphthaldehyde tosylhydrazone in benzene gave, in addition to the aldazine, 29 in 67% and 78%, respectively.

The existence of β-naphthaldazine in the reactions involving the β-naphthaldehyde tosylhydrazone sodium salt was proven by comparison of the reaction product with an authentic sample of the azine[40] which was independently synthesized.[41]

While decompositions of both carbene precursors in benzene gave the same hydrocarbon products, the decompositions of 4,5-benzotropone tosylhydrazone sodium salt in cyclohexene were unique in that there were additional products formed when compared to the β-naphthaldehyde tosylhydrazone sodium salt decompositions.

First, the pyrolysis of β-naphthaldehyde tosylhydrazone sodium salt was carried out in cyclohexene at 135-145°. The relative yields of the three volatile components are as follows: the naphthylcarbene-cyclohexene insertion product 30 (34%), the syn-norcarane 31 (26%), and the anti-norcarane

32 (40%). The aldazine was formed in 10% yield, but it is not in the above data as they only include volatile hydrocarbon products.



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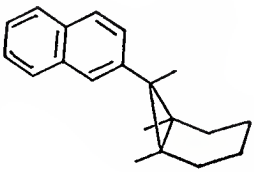

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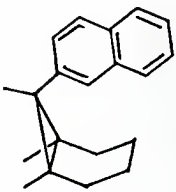

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The insertion product 30 was readily identified by nmr; the two vinylic and two "benzylic" protons were readily discernible. The syn- and anti-norcaranes required slightly more attention to effect differentiation, however. The corresponding phenylnorcarane models[42] and the guidelines put forth for their identification by Closs and coworkers[43,44] aided the characterization of the naphthyl moieties. Thus, by analogy, the syn-7-(2-naphthyl)norcarane 31 should have the naphthyl ring system facing the cyclopropane ring and this conformation would then have two separate effects on the nmr spectrum of the compound: first, several of the cyclohexyl ring protons would be held in the shielding cone of the naphthalene ring system and be consequently shifted upfield as far as 0.7 ppm compared with the anti-epimer; second, the aromatic protons would not interact with the cyclopropyl ring and their signals would be relatively narrower than the other compound. The anti-epimer 32 should exist in the conformation with the

naphthyl ring system bisecting the cyclopropyl ring[44] which would cause one of the o-protons to lie in the shielding zone of the cyclopropane ring and to be shifted upfield approximately 0.2 ppm relative to the syn-product (of course the cyclohexyl ring protons would be slightly downfield and not so broadened when compared with the former).

Second, when the sodium salt of 4,5-benzotropone tosylhydrazone was decomposed in cyclohexene heated to reflux (83°), five products were formed. These products were detected and isolated by vpc. The vpc trace of the decomposition of 4,5-benzotropone tosylhydrazone sodium salt in cyclohexene at 83° is shown in Figure 1. Two products accounted for 66% of

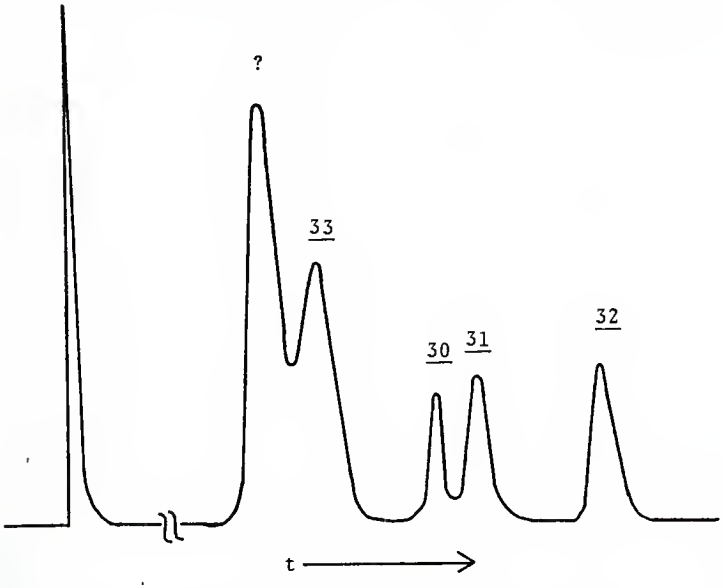

Figure 1. Vpc trace: Pyrolysis of 26 in Cyclohexene.

the material: one is unidentified, but the other has the properties of the spiro-adduct of benzocycloheptatrienylidene to cyclohexene (33). The 100 MHz nmr of 33 is shown in

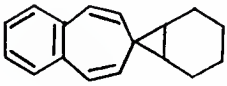

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Figure 2 and the decoupled spectrum in Figure 3. Perhaps the cyclohexyl moiety is introducing the dissymmetry present in the spectra, but it is difficult to rationalize the large differential chemical shift of the two different cycloheptatrienyl protons adjacent to the benzene ring system. The uv spectrum, λ_{max} = 240 mμ (log ε = 4.2) and 265 mμ (log ε = 3.5), compares well with that of 3,4-benzocycloheptatriene, λ_{max} = 230 mμ (log ε = 4.7) and 265 mμ (log ε = 3.7).[45] The mass spectrum of this compound indicates a molecular ion at m/e 222. The ir contributed little toward the identification except that the strong absorption at 750 cm^{-1} is indicative of an o-disubstituted benzene.[46] Also, other absorptions are present in the ir spectra of both 3,4-benzocyclohepta-1,3,6-triene[45] and the above unknown compound with approximately the same intensities (1620, 1480, 1440, 795, 745 cm^{-1} and several weak bands). The last three products and their relative yields were, respectively, (cyclophexene-3-yl)-2-naphthylmethane, the naphthylcarbene-cyclohexene insertion product, (7%), syn-7-(2-naphthyl)norcarane (12%), and anti-7-(2-naphthyl)-norcarane (15%).

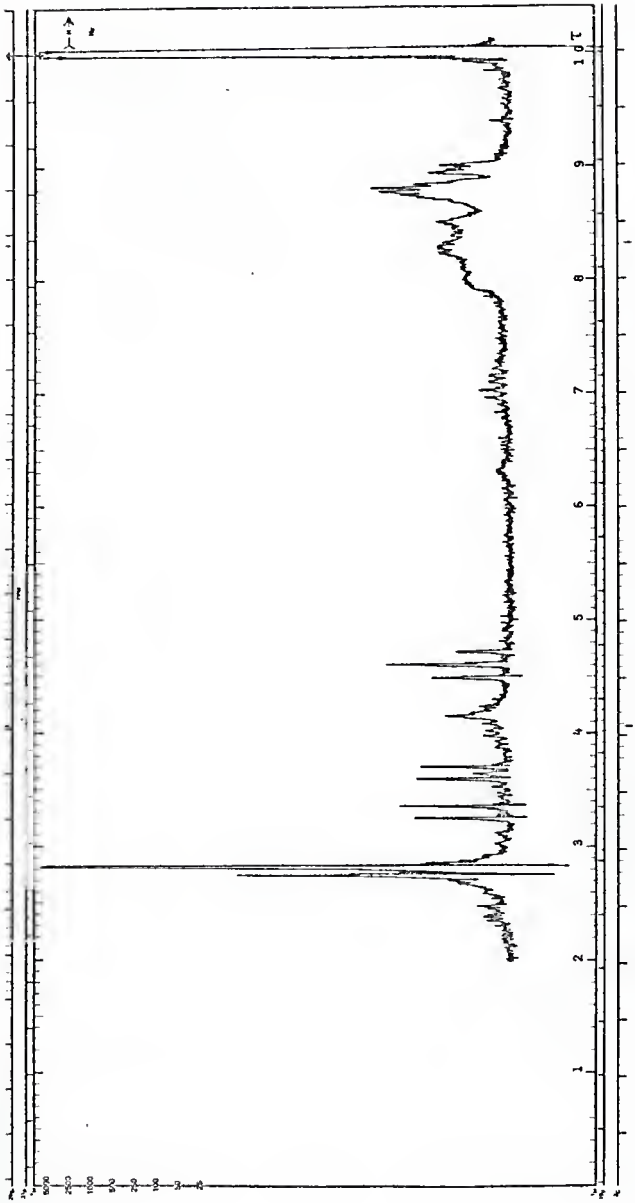


Figure 2. 100MHz Nmr of 33 (Impurities at 2.74 and 4.14 τ).

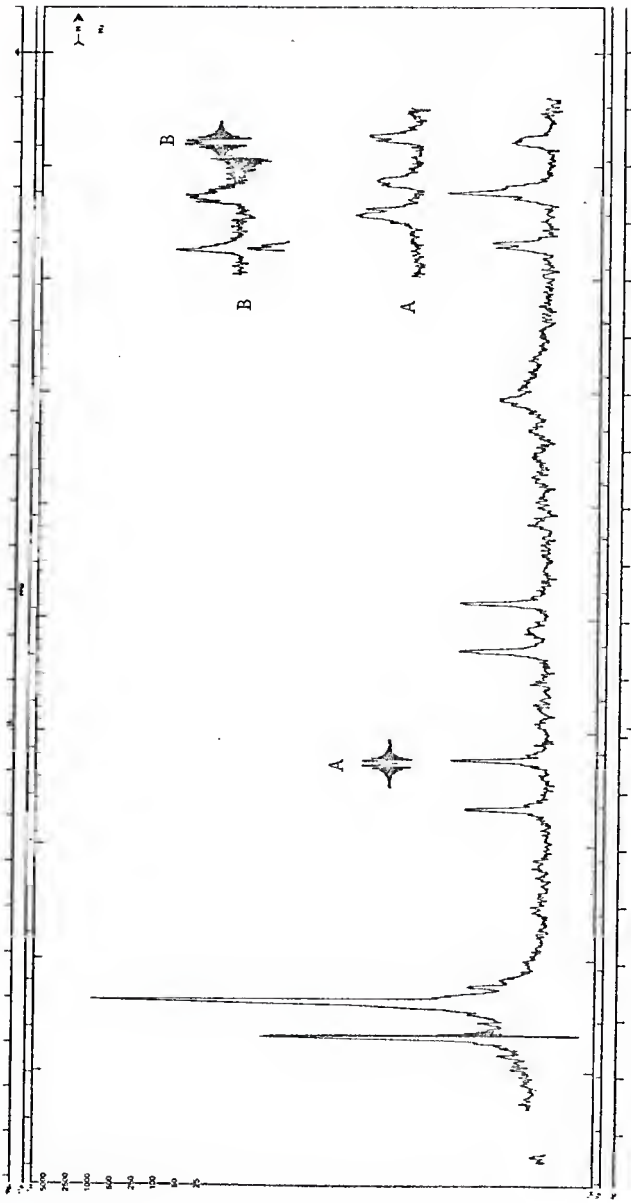


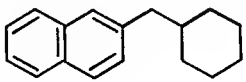
Figure 3. Decoupled Nmr of 33.

Pyrolysis of the sodium salt of 4,5-benzotropone tosylhydrazone in cyclohexene at 140° led to the same five products as the lower temperature one.

The sodium salt of 4,5-benzotropone tosylhydrazone was thermally decomposed at 82° in a 2:1 molar mixture of diglyme--cyclohexene. Analysis of the hydrocarbon products indicated the presence of the same five products as the other cyclohexene decompositions with the addition of the naphthylcarbene-diglyme insertion products. The diglyme products amounted to 27% of the total products.

Finally, the photolysis of 4,5-benzotropone tosylhydrazone sodium salt in cyclohexene at 30° produced the same products as the pyrolyses plus a new unidentified one. In the photolysis, the benzocycloheptatrienylidene addition product 33 is a major component; in the pyrolyses, the opposite is true. In the cyclohexene--diglyme reaction, interfering materials made accurate analysis impossible.

When cyclohexane was used for the substrate, the product isolated in 51% yield from the decomposition of 4,5-benzotropone tosylhydrazone sodium salt was (β-naphthyl)cyclohexylmethane (34). While the yield was not exceptional, the nmr spectrum of the crude reaction material indicated almost exclusively the insertion product and cyclohexane.



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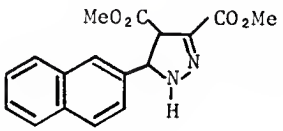
In an effort to trap the diazo compound of 4,5-benzotropone, the tosylhydrazone sodium salt was decomposed in benzene at 105-108° in the presence of an equimolar amount of dimethyl fumarate. There was considerable nitrogen evolution, and the product isolated from the reaction was the naphthylcarbene-benzene adduct 29 in 63% yield. The nmr spectrum of the crude reaction material indicated only the adduct and dimethyl fumarate. Comparative tlc, on silica gel eluted with 50:50 ethyl ether--pentane, of the known pyrazoline (vide infra) and this reaction mixture indicated no pyrazoline was present in the latter.

Naphthyldiazomethane was treated in a similar manner. The sodium salt of β-naphthaldehyde tosylhydrazone was decomposed in benzene at 105-108° in the presence of an equimolar amount of dimethyl fumarate. The product, an almost colorless, very viscous oil, had all of the properties of trans-3,4-dicarbomethoxy-5-(2-naphthyl)-2-pyrazoline (35). The oil was



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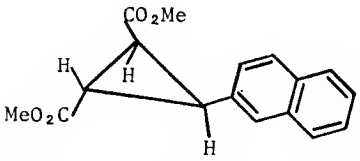
not stable to ordinary distillation conditions and even though column chromatography on silica gel effected some purification, it was not sufficient to provide a sample which gave a good elemental analysis (e.g., calcd. N, 8.97; found: N, 8.31). The ir spectrum of this compound had a strong

absorption at 3440 cm^{-1} indicative of N-H stretching, one at 1730 for the unconjugated ester carbonyl stretching, one at 1700 for the conjugated ester carbonyl, and one at 1555 indicating a C=N bond. The nmr spectrum contained absorptions at 2.10-2.60 τ indicating the naphthyl protons, a broad singlet at 3.24 τ for the proton bonded to the nitrogen, a broad doublet (J = 9.4 Hz) for the "benzylic" proton at 4.60 τ, a doublet (J = 9.4 Hz) for the proton adjacent to the carbomethoxy group at 5.92 τ, a singlet for the conjugated ester methyl at 6.18 τ, and a singlet for the unconjugated ester methyl at 6.24 τ (in addition, there were other resonances which changed in intensity depending upon work up and purification steps and were therefore not believed to originate from the pyrazoline). The trans-configuration was evident when compared with nmr data of trans-3,4-dicarbomethoxy-5-phenyl-2-pyrazoline[47] which had J = 10 Hz for the protons on C-4 and C-5 and a chemical shift of 4.87 τ for the benzylic proton on C-5. It is also interesting to note that the above phenyl pyrazoline was a viscous oil which resisted all attempts to induce crystallization.[48] The mass spectrum had no signal for the molecular ion, but there was one at 284 (the molecular ion with the loss of N_2). The λ_{max} in ethanol were 224 mμ (log ε = 4.53), 275 (3.75), and 287 (3.79). Using 2-methylnaphthalene[49] and the known 3-carbomethoxy-4-phenyl-2-pyrazoline[50] as models, the following absorptions would be expected in the uv: 223 mμ (log ε = 4.22), 274.5 (3.73), and 296 (3.98).

The decomposition of β-naphthaldehyde tosylhydrazone sodium salt in benzene at 160° in the presence of an equimolar amount of dimethyl fumarate gave rise to a different product than the low temperature one. The product was identified as trans-1,2-dicarbomethoxy-3-(2-naphthyl)cyclopropane (36) and was isolated in 67% yield. The structure was easily desig-



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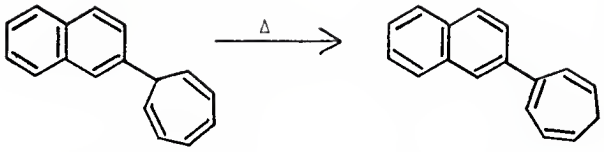
nated trans because of the two different methyl proton absorptions (either cis-cyclopropane would have had only one signal for the two methyl groups as they would be magnetically equivalent) and because the thermal decomposition of trans-3,4-dicarbomethoxy-5-phenyl-2-pyrazolines is known to give the trans-cyclopropanes.[48]

The decomposition of the sodium salt of 4,5-benzotropone tosylhydrazone in benzene at 160° in the presence of dimethyl fumarate led to the formation of 2-(2,4,6-cycloheptatrien-1-yl)-naphthalene (29) and what is believed to be 2-(2,4,6-cycloheptatrien-4-yl)naphthalene (37) in a ratio of 1.0:1.6 as determined by nmr. The latter product could arise via a [1,5] hydrogen shift of the former; the hydrogen shift product was not isolated but its presence was inferred from the nmr spectrum and from work done in the phenylcycloheptatriene series.[51]



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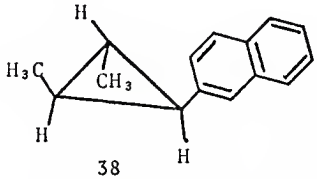
β-naphthaldehyde tosylhydrazone sodium salt was decomposed by photolysis in the presence of trans-2-butene to yield 1-(2-naphthyl)-trans-2,3-dimethylcyclopropane (38) along with a small amount of cis- and unknown materials. While other



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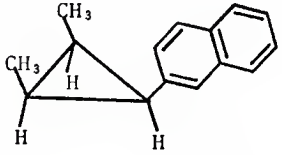
properties were consistent with this structure, the identification of this compound was hampered by the unusual nmr spectrum. The two signals arising from the methyl group protons were essentially singlets (they would be expected to be doublets). Two things were tried in order to solve this dilemma: first, the nmr spectrum was taken in a different solvent, benzene, which caused one of the singlets to split by about 1.5 Hz, and, second, the corresponding phenyl cyclopropane was prepared and its nmr spectrum examined and found to be very similar to the naphthylcyclopropane. Thus, the structure is in accord with the observed spectral properties.

The photolysis of the sodium salt of β-naphthaldehyde tosylhydrazone in cis-2-butene gave the two expected epimeric cyclopropanes along with a small amount of trans-cyclopropane and unknown materials. Syn-1-(2-naphthyl)-cis-2,3-dimethyl-



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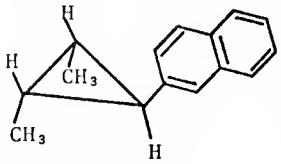

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cyclopropane (39), and anti-1-(2-naphthyl)-cis-2,3-dimethyl-cyclopropane (40) were differentiated in a manner similar to that of the epimeric naphthylnorcaranes (vide supra). In the syn-cyclopropane 39 the methyl protons appear 0.2 ppm upfield relative to the anti-compound, and the naphthyl resonances are relatively less broad. Naturally, the methyl resonances were at lower field and one of the o-protons on the naphthyl system appeared at higher field (causing a broadening of the aromatic resonances) in the anti relative to the syn.

Pyrolysis of the naphthaldehyde tosylhydrazone sodium salt in cis-2-butene gave, in addition to the epimeric cyclopropanes, an unknown product formed in considerable amounts.

When 4,5-benzotropone tosylhydrazone sodium salt was decomposed by photolysis in the presence of cis-2-butene, it gave the expected epimeric cyclopropanes, a small amount of trans-cyclopropane, and a considerable amount of unknown

material. The photolysis in trans-2-butene gave as a major product the expected trans-cyclopropane (in addition to small amounts of cis-cyclopropane and unknown material).

The pyrolysis of 4,5-benzotropone tosylhydrazone in cis-2-butene yielded large amounts of the epimeric cyclopropanes, small amounts of trans-cyclopropane, and some extraneous materials.

The stereochemistry of the addition of the carbenes to olefins was then determined by analysis of the amount of trans-cyclopropane formed in the decomposition of the two carbene precursors in research grade cis-2-butene. The decompositions were carried out under a variety of conditions. They were done using the neat olefin as solvent, they were done with the olefin diluted with benzene (1:3 molar ratio, respectively) and perfluorocyclobutane (two runs, 1:2 molar ratio and 1:6 molar ratio, respectively), and they were done with olefin in the presence of oxygen and trans,trans-2,4-hexadiene (two runs, 1.0:1.5 molar ratio and 1.0:2.1 molar ratio, respectively). Dilution had no effect upon the ratio of cis- and trans-cyclopropanes formed; however, the presence of oxygen and the diene significantly altered the above ratio, producing relatively more cis-cyclopropane. When the mole percent of trans,trans-2,4-hexadiene was greater than 66%, there was too little cis-2-butene adduct formed to determine the stereochemistry. The results of the stereochemical investigation are shown in Table 1.

TABLE 1

Stereochemical Results: The Percent "Wrong Isomer"[a] from the Decompositions in cis-2-Butene[b] of the Carbene Precursors both Thermally at 105° and Photolytically at -25°.

Tosylhydrazone Sodium Salt Solvent System (molar ratio)	% "Wrong Isomer"[c] Δ	hν
Naphthaldehyde cis-2-butene	10[d]	3
Benzotropone cis-2-butene	7	4
Benzotropone cis-2-butene/benzene (1:3)	6	
Benzotropone cis-2-butene/perfluorocyclobutane (1:2)	6	
Benzotropone cis-2-butene/perfluorocyclobutane (1:6)	6	
Benzotropone cis-2-butene/oxygen (saturated)	4	
Benzotropone cis-2-butene/2,4-hexadiene (1.0:1.5)	1	

[a] 1-(2-naphthyl)-trans-2,3-dimethylcyclopropane

[b] research grade 99.94 mole %

[c] standard deviations were typically ±1

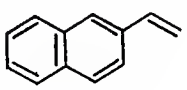
[d] datum only approximate due to interfering material

To be sure that the products were stable to vpc, the cis-cyclopropane was preparatively chromatographed and then analyzed for trans-material--none was found. Also, the olefin was analyzed after the reaction and it was found that the olefin had isomerized less than 1 percent during the course of the reaction.

In hope of sensitizing the rearrangement, the sodium salt of benzotropone tosylhydrazone was decomposed photolytically in benzene using xanthen-9-one (E_T = 74 Kcal/mole) as a sensitizer. Unfortunately, no hydrocarbon products were isolated from the reaction.

The substituted tropone, 2-methyl-4,5-benzotropone was made according to the method of Hielbronner[52] (the conversions necessary to obtain the sodium salt of the corresponding tosylhydrazone were the same as those used for 4,5-benzotropone itself).

The sodium salt of 2-methyl-4,5-benzotropone tosylhydrazone was thermally decomposed in benzene at 130° to yield two products: 2-vinylnaphthalene (41) and 2-(2,4,6-cycloheptatrien-1-yl)-3-methylnaphthalene (42). The authenticity of the



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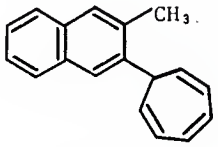

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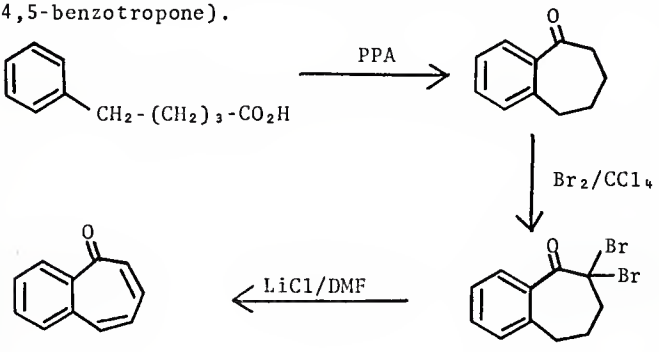
2-vinylnaphthalene from this reaction was verified by comparison of its spectral properties with those of commercially available material. The substituted cycloheptatrienylnaphthalene was identified by its spectral properties and by comparison with material obtained from the thermal decomposition of the sodium salt of 3-methyl-2-naphthaldehyde tosylhydrazone in benzene (vide infra).

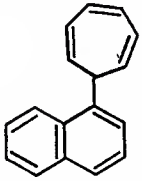
The sodium salt of 3-methyl-2-naphthaldehyde tosylhydrazone was thermally decomposed in benzene at 145° and yielded the above cycloheptatrienylnaphthalene 42 (39%) and aldazine (42%).

The products from the decomposition of the benzo precursor were analyzed by vpc and it was found that the relative ratios of the products were 2-vinylnaphthalene 72%, unknown material 6%, and 2-(2,4,6-cycloheptatrien-1-yl)-3-methylnaphthalene 22%.

Another annelated tropone, 2,3-benzotropone was prepared as shown in the scheme below[53] (again the conversions to the tosylhydrazone sodium salt were the same as those necessary for 4,5-benzotropone).



The decomposition of the sodium salt of 2,3-benzotropone tosylhydrazone in benzene at 120° gave 1-(2,4,6-cycloheptatrien-1-yl)naphthalene (43). The compound was identified by



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its spectral properties as follows: the nmr has resonances at 2.20 τ three α-protons of the naphthyl system; 2.55 τ four β-protons of the naphthyl system; 3.30 τ two protons on the 4 and 5 positions of the cycloheptatriene ring; 3.70 τ two protons on the 3 and 6 positions of the cycloheptatriene ring; 4.50 τ two protons on the 2 and 7 positions of the cycloheptatriene ring; and 6.60 τ for the one proton on the 1 position of the cycloheptatriene ring. The mass spectrum gave peaks at m/e 218 for the molecular ion, 127 for the naphthyl ring system, and 91 for the tropylium fragment. That it was the α-substituted naphthalene was shown by the ratio of the α- to β-protons in the nmr spectrum and by close examination of the ir spectrum (Cf. 2-(2,4,6-cycloheptatrien-1-yl)naphthalene); the lack of any absorptions at 861 cm^{-1} and 821 cm^{-1} and the appearance of a band at 800 cm^{-1} (for three adjacent H) and the mutual band at 745 cm^{-1} was in agreement with this structure.

CHAPTER III

DISCUSSION

To date, the interconversion of aryl and aromatic carbenes[2,6,7,9,10,12,16,18] (and nitrenes[26,28]) --such as the conversion of phenylcarbene to cycloheptatrienylidene --has been limited to the gas phase and rather high temperatures (the exceptions to this have been the ring expansion of 1,6-methano(10)annulenyl-2-carbene[15] and the small amount of rearrangement observed in the photolysis at room temperature of o-, m-, and p-methylphenylcarbenes[54]). Also, with the exceptions of aromatic carbene dimerizations and of the reaction of the expanded 1,6-methano(10)annulenyl-2-carbene with 1,2-cyclononadiene,* in no case has it been possible to examine intermolecular reactions of any of the rearranged carbenes. At this time, the rearrangement of 4,5-benzocycloheptatrienylidene to β-naphthylcarbene and that of 2,3-benzocycloheptatrienylidene to α-naphthylcarbene in solution at temperatures as low as -35° is reported. These reactions constitute examples of carbene-carbene rearrangements which are apparently not subject to either of the previous restrictions.

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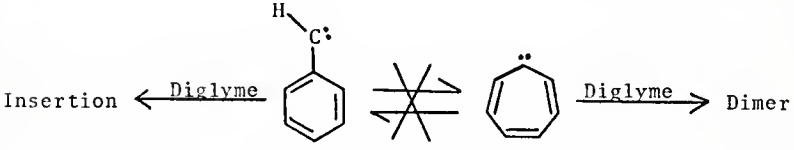
* W. M. Jones and P. H. Gebert, unpublished results.

For this study, the phenylcarbene-cycloheptatrienylidene reaction was taken as the prototype. Phenylcarbene (44) was generated in diglyme under conditions where the sodium salt of tropone tosylhydrazone gives heptafulvalene and the reaction mixture was carefully examined for cycloheptatrienylidene dimer. No trace was found. Cycloheptatrienylidene (45) was then generated under conditions where phenylcarbene gives clean reaction with solvent and the reaction mixture carefully analyzed for phenylcarbene insertion products. No trace was found.

The failure of phenylcarbene to expand in solution is probably due to a favorable competitive intermolecular reaction with solvent. Cycloheptatrienylidene, on the other



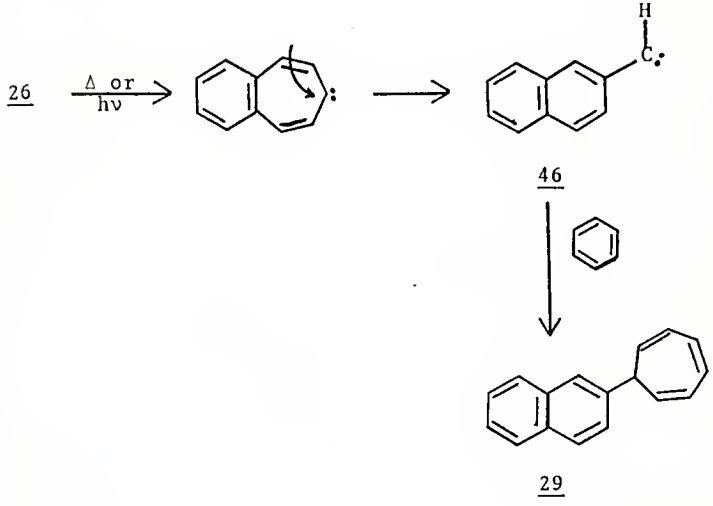
44 45

hand, is very unreactive with most solvents, preferring to simply dimerize. Thus, its failure to contract reflects an activation energy high enough to allow dimerization to dominate.

As one possible way to reduce the activation energy for contraction while hopefully retaining enough of the low reactivity of the aromatic carbene to prevent extensive reaction with solvent, benzocycloheptatrienylidene was studied. This system was chosen because monoannelation is

known to substantially decrease the stability of the tropylium ion[55] but it should have little effect upon the stability of the intermediate cyclopropene. Thus, if the stability of the carbene parallels the carbonium ion and if the rate of contraction is reflected in the relative stability of the intermediate, then benzocycloheptatrienylidene should contract faster than cycloheptatrienylidene.

The carbenes were generated from the sodium salts of the corresponding tosylhydrazones and the rearranged naphthylcarbenes were detected by their reaction products with solvent. Thus, the formation of the naphthylcycloheptatriene 29 suggests a carbene-carbene rearrangement followed by reaction of the rearranged carbene 46 with solvent. Formation of the rearranged



carbene was further supported by the formation of β-naphthylcyclohexylmethane (34) upon decomposition of the salt in cyclohexane. Considering decompositions in cyclohexene, it is interesting to note that the relative yield of the benzocycloheptatrienylidene adduct (33) appears to decrease with increasing temperature.

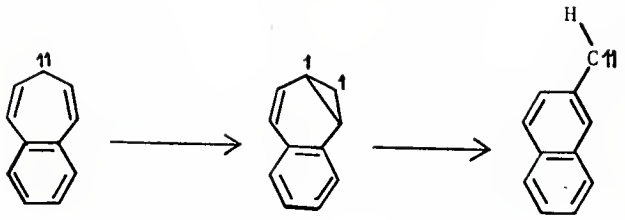
The presence of 33 and its apparent decrease with increased temperature is consistent with a bimolecular reaction of the unrearranged carbene with cyclohexene (to give 33) in competition with a unimolecular rearrangement that gives β-naphthylcarbene. Lastly, formation of the various insertion products can be taken as strong evidence[56] for formation of the rearranged carbene.

The mechanism of the carbene-carbene rearrangement, however, is quite a detailed problem. Initially, one must consider the rearrangement of a carbene precursor. Thus, the decompositions of β-naphthaldehyde tosylhydrazone sodium salt and an equivalent amount of 4,5-benzotropone tosylhydrazone sodium salt were carried out under identical conditions in the presence of an equimolar amount of dimethyl fumarate. As expected, the β-naphthyldiazomethane reaction gave as the primary product the pyrazoline. In contrast, the benzotropone tosylhydrazone salt reaction gave the now familiar benzene addition product of β-naphthylcarbene 29 with no detectable trace of the pyrazoline 35. When the reactions were carried out at higher temperatures, the former yielded the 1,2-dicarbomethoxy-3-naphthylcyclopropane 36 and the latter gave,

in addition to the usual β-naphthylcarbene-benzene adduct, a new product 37. The nmr of the unisolated material suggests that it is the thermal (1,5) hydrogen shift product of the original adduct. All of the above data are consistent with the rearrangement occurring via a carbene, not a carbene precursor.

Once it was determined that a carbene was probably the rearranging species, it became necessary to differentiate between rearrangement occurring from the singlet state and that from the triplet state and knowledge of the multiplicity of the initial carbene was imperative. In principle, this facet of the problem may be explored by investigating the stereochemistry of the addition of rearranged β-naphthylcarbene to olefins. Stereospecific addition is taken as strong evidence for the reaction of the singlet state, whereas the triplet state appears to add nonstereospecifically.[57,58] Furthermore, the ground state of β-naphthylcarbene has been shown to be triplet.[59] Thus, a high degree of stereospecific addition would point to the singlet as the reacting species (unless the singlet and triplet are in equilibrium --this will be discussed below).

The rearrangement via the triplet state might occur as shown in the scheme below (this is simply a diradical form of the cyclopropene mechanism, vide infra).



Photolytically, in the pure olefin, β-naphthylcarbene from both precursors gave 96-97% stereospecificity which is in good agreement with the work of Closs[43] who found 95-97% stereospecificity with phenylcarbene in pure olefins.

Thermally, the stereospecificity was less than the corresponding photochemical reactions (ca. 93%); this may be because of a thermal dependence of intersystem crossing.[57] It is in agreement with the amount of nonstereospecificity observed in the addition of thermally generated dicyanocarbene to cis-2-butene (8% in neat olefin), however, singlet-to-triplet transition in dicyanocarbene is competitive with addition, and thus the stereospecificity is sensitive to dilution effects.[60]

The dilution effect is caused by the different concentration dependence of intersystem crossing and addition to the olefin; the former is unimolecular and the latter, of course, is dependent upon olefin concentration.[57] When applied to the naphthylcarbene system, dilution either with benzene or octafluorocyclobutane had no effect upon the stereospecificity.

Another experimental test for multiplicity is scavenging of paramagnetic species by oxygen or dienes. As Closs states,[57] the stereospecificity should be increased in the presence of a diene (if the triplet is not in rapid equilibrium with the singlet) because the scavenging of the paramagnetic species "results in a correspondingly greater proportion of the singlet-state reaction." Thus, when the β-naphthylcarbene is generated from the salt of 4,5-benzotropone tosylhydrazone in the presence of olefin and oxygen, the addition is somewhat more stereospecific. By making some approximations from existing data,[61] namely that the solubility of oxygen in benzene is similar to that of butene and that the solubility is a linear function of temperature, a saturated solution of 120 millimoles of butene should contain ca. 0.2 millimoles of oxygen under reaction conditions. This concentration was apparently sufficient to increase the stereospecificity by 2% (which was also the amount it was increased when applied to the fluorenylidene system by M. Jones, Jr.).[62]

Furthermore, more effective scavenging was accomplished by utilizing trans,trans-2,4-hexadiene. In this case the effect was pronounced in that the stereospecificity was increased to 99%. In the hexadiene experiments, a large part (ca. 90%) of volatile product was apparently from reaction with the diene (relative to the amount of reaction with butene as determined by vpc). This is quite in line with the data of Moss[58] who, using similar conditions, reported that approximately 70% of the reaction product

appeared to be derived from the reaction of phenylcarbene with the diene.

In summary, the β-naphthylcarbene added to olefins with a high degree of stereospecificity which was unchanged by dilution but was increased by the addition of triplet scavengers. These data are compatable with a scheme in which there is a thermally driven singlet-triplet equilibrium wherein the stereospecificity is independent or only slightly dependent upon olefin concentration. If there is a rapid singlet-triplet equilibrium, one can no longer be assured that the singlet is the rearranging species. The rearrangement could be occurring via the triplet state, but since there is an equilibrium it might not be reflected in the stereochemistry.

These data appear inconsistent with a scheme in which intersystem crossing is in effective competition with addition of the singlet to olefins as in the case of fluorenylidene.[62] The stereospecificity of addition of fluorenylidene to olefins is dependent upon both the concentration of olefin and the addition of triplet scavengers. They are also incompatible with a scheme where there is a rapid singlet-triplet equilibrium in which the stereospecificity is unaffected by the addition of triplet scavengers (as in the case of diphenylcarbene).[57]

Initially it seems that a dicotomy exists, but one can envision a system whereby all of the above facts can be readily explained and which leaves little doubt but that the initially formed β-naphthylcarbene is a singlet.

The following scheme indicates the effects of changing the concentrations of diene and olefin upon cis- and trans-cyclopropane ratio; the explanation of symbols is as follows:

B = benzocycloheptatrienylidene

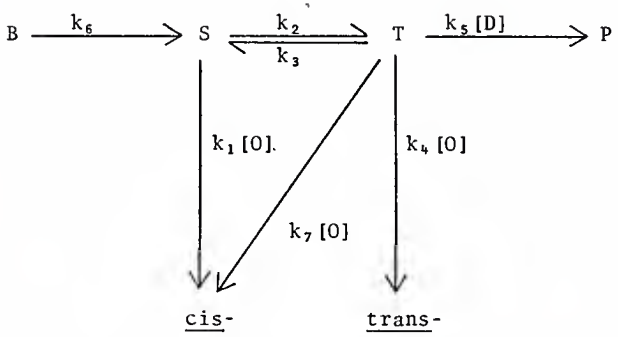
S = singlet naphthylcarbene

T = triplet naphthylcarbene

D = diene (2,4-hexadiene)

O = cis-2-butene

P = diene-carbene products



$$\frac{d\ cis}{dt} = k_1[O][S] + k_7[O][T] \qquad \frac{d\ trans}{dt} = k_4[O][T]$$

$$\frac{\frac{d\ cis}{dt}}{\frac{d\ trans}{dt}} = \frac{k_1[O][S] + k_7[O][T]}{k_4[O][T]}$$

Integrate over all time and assume the right-hand side to be constant.

$$\frac{cis}{trans} = \frac{k_1[O][S] + k_7[O][T]}{k_4[O][T]} = \frac{k_1[S]}{k_4[T]} + \frac{k_7}{k_4} \qquad (1)$$

Assume a steady-state concentration for [T] which is "particularly good when the intermediates are very reactive and, therefore, present at very small concentrations."[63]

$$\frac{d[T]}{dt} = k_2[S] - k_3[T] - k_4[O][T] - k_7[O][T] - k_5[D][T] = 0$$

$$[T] = \frac{k_2[S]}{k_3 + k_4[O] + k_7[O] + k_5[D]} \qquad (2)$$

Substitute for [T] from eq. (2) into eq. (1) and simplify

$$\frac{cis}{trans} = \frac{k_1k_3 + k_1k_4[O] + k_1k_7[O] + k_1k_5[D] + k_2k_7}{k_2k_4}$$

If there is a rapid equilibrium, $k_3 >> k_4[O]$, $k_7[O]$, $k_5[D]$ and $k_2 >> k_1[O]$.

Then $\frac{cis}{trans} = \frac{k_1k_3}{k_2k_4}$ (3)

and, the ratio is independent of olefin and diene concentrations.

If the reaction is irreversible, $k_4[O] >> k_3$, $k_7[O] >> k_3$. Disregard the diene for first case.

Then $\frac{cis}{trans} = \frac{k_1(k_4 + k_7)[O] + k_2k_7}{k_2k_4}$

and the ratio is dependent upon olefin concentration.

Now include the diene in the scheme $k_4[O] >> k_3$, $k_7[O] >> k_3$, and $k_5[O] >> k_3$.

$$\frac{cis}{trans} = \frac{k_1k_5[D] + k_1(k_4 + k_7)[O] + k_2k_7}{k_2k_4} \qquad (4)$$

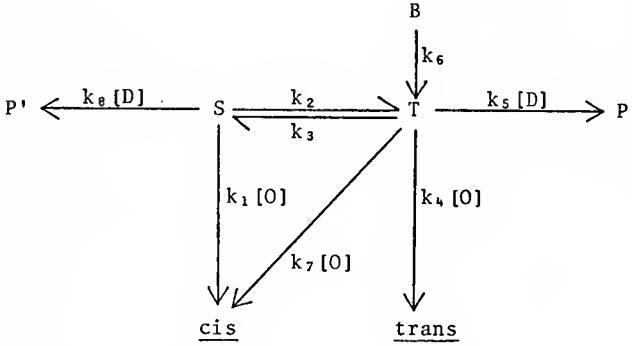
and the ratio is dependent upon diene and olefin concentrations.

If, however, $k_3 >> k_4[O]$, $k_3 >> k_7[O]$, but $k_5[D] >> k_3$ then

$$\frac{\text{cis}}{\text{trans}} = \frac{k_1k_5[D] + k_2k_7}{k_2k_4} \qquad (5)$$

and the ratio is dependent only upon the diene concentration.

One must consider, however, that the rearrangement might be going via the triplet benzocycloheptatrienylidene (one need not concern oneself with triplet benzocycloheptatrienylidene rearranging to singlet naphthylcarbene). Thus, the scheme below indicates entry into the triplet rearranged carbene.



$$\frac{d\ \text{cis}}{dt} = k_1[O][S] + k_7[O][T] \qquad \frac{d\ \text{trans}}{dt} = k_4[O][T]$$

Integrate as in the first case

$$\frac{\text{cis}}{\text{trans}} = \frac{k_1[O][S] + k_7[O][T]}{k_4[O][T]} = \frac{k_1[S]}{k_4[T]} + \frac{k_7}{k_4}. \qquad (6)$$

Assume a steady-state concentration of [S].

$$\frac{d[S]}{dt} = k_3[T] - k_2[S] - k_1[O][S] - k_8[D][S] = 0$$

$$[S] = \frac{k_3[T]}{k_2 + k_1[O] + k_8[D]} \qquad (7)$$

Substitute [S] from eq. (7) into eq. (6) and simplify.

$$\frac{cis}{trans} = \frac{k_1 k_3}{k_4(k_2 + k_1[O] + k_8[D])} + \frac{k_7}{k_4} \qquad (8)$$

If $k_8[D] >> k_2$, but $k_2 >> k_1[O]$ then

$$\frac{cis}{trans} = \frac{k_1 k_3}{k_4 k_8 [D]} + \frac{k_7}{k_4} \qquad (9)$$

and the ratio is inversely proportional to the diene concentration.

Finally, one might envision a scheme wherein the benzocycloheptatrienylidene is the intermediate which undergoes the singlet-triplet intersystem crossing. Each state of the unrearranged carbene then yields the corresponding β-naphthylcarbene as shown in the scheme below; the explanation of symbols is as follows:

B^S = singlet benzocycloheptatrienylidene

B^t = triplet benzocycloheptatrienylidene

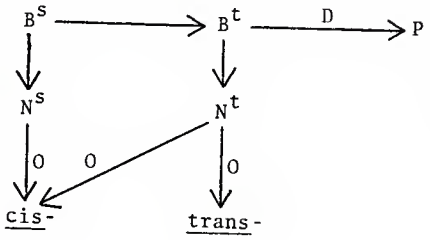
N^S = singlet naphthylcarbene

N^t = triplet naphthylcarbene

D = diene

O = cis-2-butene

P = diene-carbene products



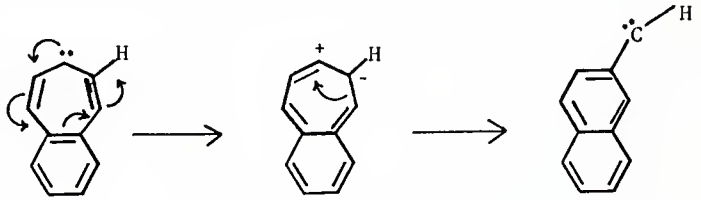
There would be no dilution effect because intersystem crossing and rearrangement are both unimolecular; the scavenging effect would arise from reaction of diene with the unrearranged carbene. In agreement with the arguments above, the singlet still must be the state by which most of the rearrangement occurs in order to explain the high degree of stereospecificity observed.

Excluding the benzocycloheptatrienylidene intersystem crossing, what is required for the explanation of the facts concerning the stereospecificity of β-naphthylcarbene addition is that the rate of triplet-singlet intersystem crossing proceeds at a rate considerably greater than those of the additions of the triplet carbene to the mono-olefin. Also, the rate of triplet addition to the diene (and oxygen) must be greater than the rate of triplet-singlet intersystem crossing. Accordingly, it has been reported that diphenylcarbene reacts with 1,3-butadiene more than one hundred times faster than unconjugated olefins.[64] The above kinetic scheme depicts the desired situation in eq. (5) and is also compatible with the earlier situations of fluorenylidene as shown in eq. (4) and diphenylcarbene as shown in eq. (3). It also vitiates the mechanism whereby the triplet is the rearranging species because the addition of diene would be required to decrease the cis-trans ratio as shown in eq. (9).

With the triplet pathway ruled out, at least four mechanisms have been considered which arise from the singlet state of the unrearranged carbene. The singlet mechanisms

are a carbocyclic version of the Wolff rearrangement, a Skattebol-type rearrangement, that going via a fused cyclopropene intermediate, and a concerted rearrangement.

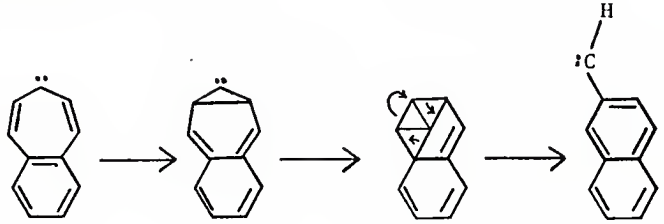
The Wolff-type rearrangement (or perhaps more accurately the "retro-Wolff" rearrangement) is shown below. This



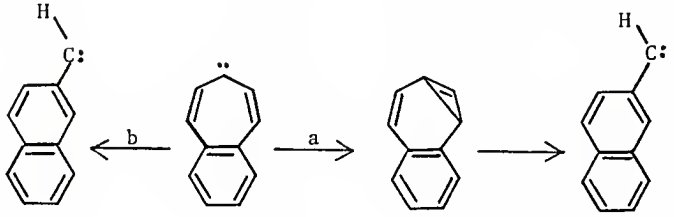
mechanism is not very favorable for two reasons. First, annelation should retard it because of loss of aromaticity in the benzene ring. Second, Jones and Mitsuhashi have postulated that the Wolff and the cyclopropene mechanisms would differ experimentally in that the latter mechanism should be favored by high double bond character whereas the Wolff mechanism should be retarded.[14] Their work on the importance of bond order in the interconversion of aryl and aromatic carbenes by studying the gas-phase, carbene-carbene rearrangement of a series of substituted naphthylcarbenes, showed that net cleavage of bonds of high bond order is observed; net cleavage of bonds of low bond order is not. Thus, the evidence mitigates against a Wolff mechanism.

Another mechanism which can be written for the contraction of cycloheptatrienylidene (and also for benzocycloheptatrienylidene) is essentially the Skattebol[1] vinylcyclopropyli-

dene-cyclopentenylidene rearrangement with cleavage of different bonds. However, the effect of annelation argues against this possibility since it should retard norcaradiene formation (to prevent loss of aromaticity) and hence the rate of contraction.



The differentiation of the mechanisms involving the fused cyclopropene (route a) and the concerted pathway (route b) present a subtle problem. In fact, unless the benzobicycloheptatriene intermediate can be trapped or observed (spectroscopically, etc.) there can be no real distinction between the two. If the reaction is not concerted, the activation



energy for ring opening must be quite low* as evidenced by the fact that benzobicycloheptatrienylidene contracts to β-naphthylcarbene at temperatures as low as room temperature. The low activation energy is not unreasonable since the energy lost in cleaving the single bond of the twisted cyclopropene (the benzobicycloheptatrienylidene) might well be of the same order of magnitude as the naphthyl resonance energy gained. In the model system it has been suggested that "relatively small energy barriers separate phenylcarbene, cycloheptatrienylidene, and bicycloheptatrienylidene isomers."[12]

For the discussion of a detailed mechanism of the rearrangement it will be assumed that the process occurs via the fused cyclopropene intermediate since this facilitates the dissection of the problem and because it seems intuitively likely that the cyclopropene is a distinct intermediate.

Accordingly, Bergman[66] recently reported that the thermal isomerization of a substituted cyclopropene very likely went through a vinylcarbene intermediate. He gave no suggestions as to the pathway of ring opening and closure except to rule out a "diradical" mechanism.

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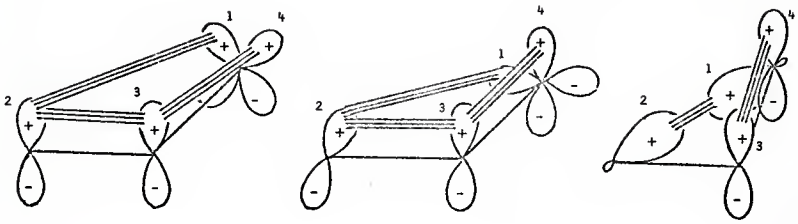
* Assuming that the intermediate has a half-life of 0.1 sec and that the pre-exponential factor (A) is similar to that for cyclopropene opening,[65] a value of ca. 15 Kcal/mole is found for the energy of activation at 27°.

Thus while the preferred conformation for closure of vinylcarbenes to cyclopropenes is unknown, it may occur from a structure in which the filled orbital of the carbene is orthogonal to the π-system which was suggested by Closs[67] and by calculations which imply that this should be the conformation of the ground-state singlet of vinylcarbene.[68]

Using Zimmerman's[69] MO Following approach to correlation diagrams, one can arrive at the preferred conformation of the rearranging (or rearranged) carbene. This approach is applied to cases where there is no element of symmetry and which consist of a linear array of orbitals. Considering benzocycloheptatrienylidene and treating the system as a vinylcarbene-cyclopropene addition, the remainder of the benzenoid system is disregarded (the subsequent ring opening is just the reverse of the addition). Application of Zimmerman's "four basic rules" yields the correlation diagram shown in Figure 4. It is immediately obvious that $p_1 - p_4$ is the occupied orbital (in the singlet state) and, since it accepts the electron pair, it will have added s character. The final result is that of the benzocycloheptatrienylidene with the vacant orbital vertically oriented $(p_1 + p_4)$ and conjugated with the π-system, and the orbital containing the non-bonded electrons, $s + (p_1 - p_4)$ weighted, horizontally oriented in a plane containing the sigma framework.



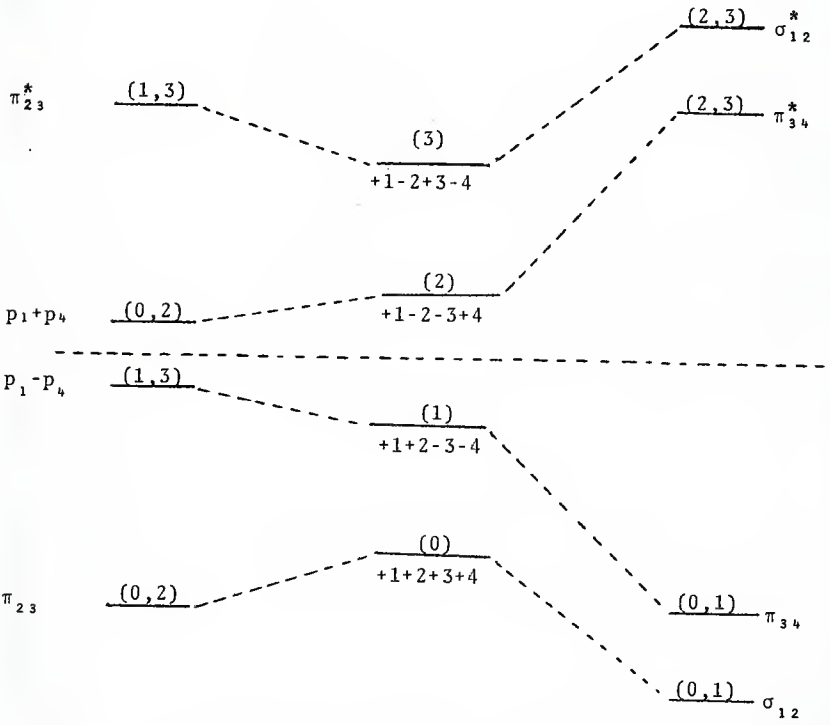
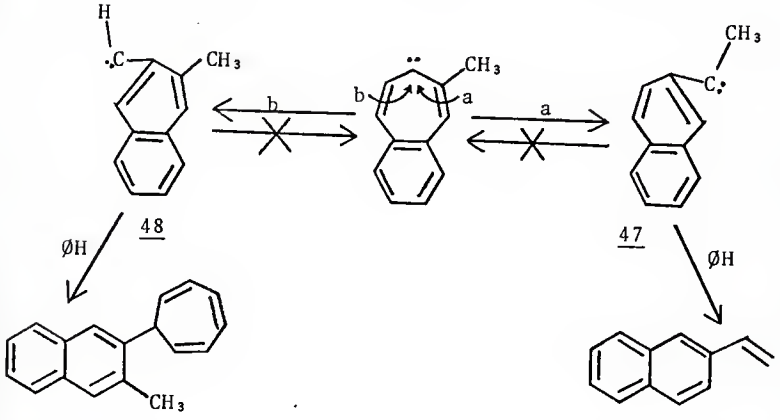


Figure 4. Closure of Vinylcarbene to Cyclopropene.

In hope of elucidating the mechanism somewhat, the effect of methyl substitution upon the rate of carbene-carbene rearrangement was cursorily examined. From the preferred formation of 41 versus that of 42 in the decomposition of the sodium salt of 2-methyl-4,5-benzotropone tosylhydrazone in benzene, it appears that alkyl substitution favors rearrangement. The validity of this conclusion



42 41

rests on the fact that neither 3-methyl-2-naphthylcarbene (48) nor methyl-2-naphthylcarbene (47) ring expands under the reaction conditions and thus indicates that both reactions are irreversible.* It is recognized that this datum will not enable one to pinpoint a single mechanism, but in order

* From the product distribution, the free energy difference between the two product transition states is on the order of 1 Kcal/mole at 130°.

to explain it, attention must be focused on some interesting concepts about this general type of rearrangement. In dissecting this problem, two types of interactions or conformations must be considered: a boat-shaped system wherein the ring containing the carbene center is puckered and delocalization of π-electrons into the carbene p orbital is minimal, and a planar system with delocalization of π-electrons into the vacant p orbital of the carbene (similar to cycloheptatrienylidene[8] which calculations imply has a planar structure).* In each of these two conformations, one must examine three effects: steric, geometric, and electronic.

Models suggest that steric effects are unimportant since in neither conformation is the methyl group able to significantly aid in the formation of the transition state by lessening any non-bonded interactions.

The transformation from the boat conformation (Figure 5) could be envisioned as occurring by interaction of the empty

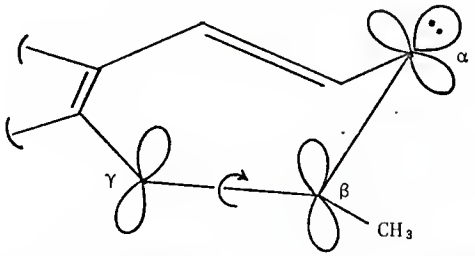


Figure 5. Boat Conformation of Benzocycloheptatrienylidene.

* J. Sabin, Physics Department, University of Florida, personal communication.

p orbital of the carbene with the rotating p orbital of the γ-carbon to form the new sigma bond and by interaction of the sp^2 orbital of the carbene with the p orbital of the β-carbon to yield the twisted cyclopropene double bond.

From an examination of models, it appears that in the boat conformation there is very good orbital orientation for efficient overlap. Thus, it seems readily adapted to the formation of a fused, twisted cyclopropene (i.e., the ground state geometry of the boat form closely resembles that of a possible transition state). It is quite possible that the boat form is the lower energy conformation in this system in spite of the assumption that the benzotropylium cation has a planar structure.[70] However, coplanarity is not requisite as the activation energy for the rearrangement may include the energy necessary for the planar system to become puckered.

In the planar case (Figure 6), the cyclopropene sigma bond would be formed by the interaction of the back lobe of the inverting sp^2 orbital on the carbene carbon with the rotating p orbital on the γ-carbon. Localization of a pair

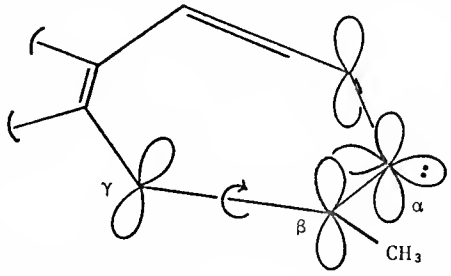


Figure 6. Planar Conformation of Benzocycloheptatrienylidene.

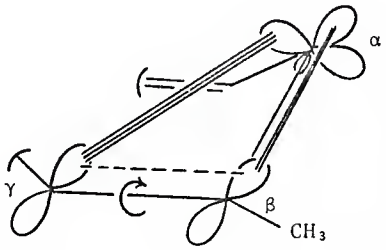
of π-electrons in the still conjugated p orbitals of the α- and β-carbons would then form the new double bond (in a manner similar to the nucleophilic attack of carbenes upon electron-deficient double bonds).[8]

The planar form has to rehybridize to accomplish the inversion at the carbene center (this is not required of vinylcarbene cyclization). From examination of models, this rehybridization introduces strain into the ring before there is what appears to be good orbital overlap; this could increase the energy of activation for closure. That is, in contrast to the boat form, in this case there seems to be less initial interaction leading to the rehybridization in that initially the two potentially interacting orbitals are orthogonal.

The published electron effects are obscure and, consequently, lend very little aid to differentiation of the two modes of attack. Closs attributes alkyl substitution effects to the possibility of both steric and electronic components in the formation of cyclopropenes from the ring closure of vinylcarbenes;[67] it appeared, though, that the steric portion was dominant. Closs also observed that an alkyl group in the olefinic position of the cyclopropene was considerably less effective in its ability to stabilize the cyclopropene than alkyl groups at the saturated center.[71]

From an examination of possible electronic effects in the boat conformation, it appears that in the formation of the transition state of the rearrangement the β-carbon acquires a partial positive charge. This charge deficiency

could arise from loss of conjugation with the p orbital of the γ-carbon due to the latter's rotation toward the carbene center. What the electron deficiency requires is a greater degree of bond breaking between β- and γ-carbons than bond formation between the α- and β-carbons (shown below) which



is not unlike the unequal bond formation predicted for the electrophilic addition of carbenes to double bonds.[72] It is known that alkyl substitution facilitates this type of addition.[73]

Unfortunately, one cannot make conclusive predictions about the electronic effects of the methyl group in the planar conformation. There is the possibility, though, that the methyl group would have little or no effect upon the rate of the rearrangement. Thus, concerning the closure of vinylcarbenes to cyclopropenes, Closs[67] stated that with progressive rotation of the γ-carbon there was the possibility of a decrease of π-electron density at that site due to the formation of the double bond between the α- and β-carbons

(implying little change in electron density at the β-carbon). Using the same reasoning, it would appear that there would be little or no charge deficiency on the methyl-substituted β-carbon of the planar system resulting in little or no effect by the methyl group on the rearrangement.

It should now be pointed out that while geometric and electronic effects do not form any real basis for prediction of a preferred pathway, they are certainly consistent with the "electrophilic-like" type of interaction discussed earlier. Thus, the prediction of Closs and the calculations of Zimmerman need not be incorrect as vinylcarbene may rearrange in the manner described by them. But, carbocyclic, aromatic carbenes may well rearrange by the other pathway due to electronic effects brought about by geometric constraints. For example, the apparent similarity of the boat form to a possible transition state, and, in contrast to the assumed geometry for the closure of vinylcarbenes,[67] the geometry of cycloheptatrienylidenes is such that the sp^2 orbital of the carbene is trans- to the double bond.

A clue to the reason for the rather dramatic effect of annelation on the ease of ring contraction may be found in the effect of annelation on the pK_{R+} values of model cations.[55] Carbonium ions should be fair models for these carbenes since, in aromatic carbenes, the vacant orbital is probably conjugated with the π-system with the non-bonded pair of electrons in the plane of the sigma framework.[74] The tropyl cation has a value of 4.7 and the benzotropyl cation has a value of 1.7.

Annelation would not be expected to substantially change the stability of the intermediate, but annelation of the tropyl cation causes a marked decrease in the pK_{R+} signaling a substantial destabilization. Thus, the energy of activation for ring contraction should be less in the annelated system than in the nonannelated one.

von R. Schleyer* has done "back of the envelope" calculations on the "strain energy" on phenylcarbene, cycloheptatrienylidene, and the bicycloheptatriene and come to the conclusion that they are all of similar energy. Thus, it appears reasonable that even modest annelation effects could be enough to cause the energetics of the annelated system to favor ring contraction over the ring expansion exhibited in the cycloheptatrienylidene series.

Lastly, in order to test the generality of the benzocycloheptatrienylidene-naphthylcarbene rearrangement, the sodium salt of 2,3-benzotropone tosylhydrazone was decomposed in benzene to yield the α-naphthylcycloheptatriene. The smooth rearrangement fits perfectly into the overall picture of the rearrangement.

In summary, benzocycloheptatrienylidenes rearrange to naphthylcarbenes in solution thermally at temperatures in the range of 100° and photolytically at temperatures as low as -35° with the rearranged carbenes being detected by their reaction products with solvent. The rearrangement may occur

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* P. von R. Schleyer, Princeton University, personal communication.

via a fused cyclopropene intermediate from the boat form of the singlet unrearranged carbene, from the planar form of the singlet, or via a concerted pathway.

CHAPTER IV

EXPERIMENTAL

General.--Melting points were taken in a Thomas-Hoover Unimelt apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia. Ultraviolet spectra (uv) were recorded on a Cary 15 double-beam spectrophotometer using 1 cm silica cells. Infrared spectra (ir) were recorded with a Beckman IR10 with absorptions reported in reciprocal centimeters. In all cases where the KBr pellet technique was not used, sodium chloride plates were substituted. Nuclear magnetic resonance spectra (nmr) were determined on a Varian A-60A high resolution spectrometer or a Varian XL 100 spectrometer. Chemical shifts are reported in tau (τ) values from internal tetramethylsilane standard. Mass spectra were determined on a Hitachi model RMU-6E mass spectrometer.

Analytical thin-layer chromatography (tlc) was accomplished on 2 in x 8 in plates coated in these laboratories with 0.25 mm layers of E. Merck HF-254 silica gel. Components were visualized by their quenching of fluorescence under uv light. Vapor phase chromatography (vpc) was carried out using a Varian Aerograph 90-P thermal conductivity instrument using column A (18 ft x 0.25 in in 20% SE-30 on Chromosorb W at 210°) or column B (3 ft x 0.25 in 15% SE-30 on Chromosorb W at 190°) and a Varian Aerograph Series 1200 flame ioniza-

tion instrument using column C (9 ft x 0.125 in 5% SE-30 on Chromosorb W at 155°). The analytical technique for determining product ratios from vpc data was that of cutting and weighing. All chemicals were reagent grade unless otherwise stated. Diglyme (diethylene glycol dimethyl ether) and tetrahydrofuran were dried by passage over activity grade I Woelm alumina and subsequent storage over CaH_2. The analyzed research grade cis-2-butene was from Matheson Gas Products, Inc. (cis-2-butene, 99.94%; trans-2-butene, 0.04%; and butadiene, 0.02%).

Pyrolysis of the Sodium Salt of Benzaldehyde Tosylhydrazone in Diglyme.--To 30 ml of dry diglyme in a 3 oz Fischer-Porter Aerosol Compatibility Tube was added 0.10 g (0.34 mmol) of the sodium salt of benzaldehyde tosylhydrazone.[38] The sealed tube was placed in an oil bath preheated to 165° for 30 min. At the end of this time all trace of color of the diazo was gone, leaving the solution colorless. The mixture was allowed to cool, poured into water (200 ml), and extracted with pentane (three 30 ml portions). The combined pentane extracts were washed with water (three 50 ml portions), dried ($MgSO_4$), and concentrated on a rotary evaporator under reduced pressure. The nmr spectrum of the residue, a light yellow oil, indicated no heptafulvalene was present, only what is believed to be the phenylcarbene-diglyme adducts. The nmr ($CDCl_3$) showed τ 2.80 (phenyl protons) and 6.5 (diglyme protons). In addition, there was aldazine produced in the reaction. Comparative tlc of the residue with a

known sample of heptafulvalene was carried out using silica gel eluting with pentane. This confirmed the absence of heptafulvalene in the reaction products.

Pyrolysis of the Sodium Salt of Tropone Tosylhydrazone in Diglyme.--Into a Carius tube was placed 80 mg (0.27 mmol) of the sodium salt of tropone tosylhydrazone[8] and 10 ml of dry diglyme. The sealed tube was immersed in an oil bath preheated to 210° and allowed to remain for 30 min. Upon cooling, the tube was opened and the contents poured into water (120 ml) and extracted with pentane (three 33 ml portions). The combined pentane extracts were washed with water (three 50 ml portions) and dried ($MgSO_4$). The dry pentane solution was concentrated on a rotary evaporator under reduced pressure to yield a very dark solid. The nmr spectrum of the residue was identical to that of heptafulvalene with a small amount of aromatic resonance at 7.2 τ, but none at 6.2-7.0 τ (the position expected for any diglyme insertion products).

4,5-Benzotropone.--The 4,5-benzotropone used in this research was prepared by the method of Thiele and Weitz[33] with the exception that a steel high pressure reactor was used in place of a sealed glass tube.

4,5-Benzotropone Tosylhydrazone.--In a typical run, 2.00 g (0.013 mol) of 4,5-benzotropone, 2.38 g (0.013 mol) of p-toluenesulfonylhydrazide, and 2 drops of conc sulfuric acid were placed in 55 ml of 95% ethyl alcohol and heated at

reflux for 1 hr. Upon cooling, 4,5-benzotropone tosylhydrazone precipitated from the solution and was isolated by filtration. Recrystallization from absolute ethyl alcohol yielded 2.5 g (51%) of the product. There were two crystal forms of the tosylhydrazone: red plates (mp 186-189°) and yellow needles (mp 180-185°). The other properties of the tosylhydrazone were as follows: ir (KBr) 3200, 1638, 1325, 1165, 575, 555 cm^{-1}; nmr (acetone-d_6) τ 2.00-2.80 (A_2B_2, 4H, J=8, toluyl aromatic), 2.62 (s, 4H, benzo), 2.90-3.80 (m, 4H, cycloheptatrienyl), 7.60 (s, 3H, toluyl methyl); mass spectrum 324 (M+).

Anal. Calcd. for $C_{18}H_{16}N_2O_2S$: C, 66.64; H, 4.97; N, 8.64; S, 9.89. Found: C, 66.52; H, 5.07; N, 8.57; S, 9.97.

β-Naphthaldehyde Tosylhydrazone.--In a typical run, β-naphthaldehyde (Aldrich Chemical Co.), an equivalent amount of p-toluenesulfonylhydrazide, and a few drops of conc HCl were placed in 95% ethyl alcohol and allowed to stir overnight at room temperature and the resulting crystals filtered and recrystallized from ethyl alcohol to give the tosylhydrazone. The product had a mp 175°, lit.[36] 174°.

General Preparation of the Sodium Salts of Tosylhydrazones.--The sodium salts were prepared by dissolving the tosylhydrazone in dry THF and adding one equivalent of sodium hydride (57% in mineral oil - Alfa Inorganics) slowly with stirring. The mixture was allowed to stir for 1 hr. At the end of this period, pentane was added to precipitate the

sodium salt (this was not always necessary). The salt was filtered, washed with additional pentane, and dried. The entire operation was carried out in a dry box, although some of the salts seemed to be stable to laboratory conditions.

Pyrolysis of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone in Diglyme.--To 13 ml of dry diglyme in a 3 oz Fischer-Porter Aerosol Compatibility Tube was added 0.45 g (1.3 mmol) of the sodium salt of 4,5-benzotropone tosylhydrazone. The sealed tube was placed for 20 min in an oil bath which had been preheated to 100°. At the end of this time 78% of the theoretical amount of nitrogen had been evolved. The reaction mixture was allowed to cool, poured into water (200 ml), and extracted with pentane (three 30 ml portions). The combined pentane extracts were washed with water (three 50 ml portions), dried ($MgSO_4$), and concentrated on a rotary evaporator under reduced pressure. The remaining yellow oil was chromatographed on alumina and eluted with ethyl ether to yield 103 mg (29%) of the naphthylcarbene-diglyme insertion products. Although the yield was only 29%, the nmr spectrum of the crude reaction mixture showed mainly diglyme and the adducts. The adducts had the following properties: ir (film) 3050, 2920, 2880, 1600, 1450, 1100, 860, 820, and 750 cm^{-1}; nmr ($CDCl_3$) τ 2.00-2.80 (m, 7H, naphthyl), 6.10-7.20 (m, 15H, diglyme and benzylic); mass spectrum 274 (M+).

Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08; O, 17.49. Found: C, 74.59; H, 8.05; O, 17.36.

The sodium salt of β-naphthaldehyde tosylhydrazone was thermally decomposed and worked up in a manner analogous to the above pyrolysis. The naphthylcarbene-diglyme adduct was isolated in 13% yield; the major product was naphthaldazine. The adduct's nmr spectrum was identical to that of the products from the pyrolysis of the sodium salt of 4,5-benzotropone tosylhydrazone (vide supra).

Photolysis of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone in Diglyme.--To 15 ml of dry diglyme in a photolysis vessel which consisted of a Pyrex tube with a side arm and equipped with a small mechanical stirrer, was added 250 mg (0.72 mmol) of the sodium salt of 4,5-benzotropone tosylhydrazone. The mixture was rapidly stirred and the photolysis carried out by mounting the apparatus vertically alongside and as close as possible to a 550 watt Hanovia medium pressure mercury lamp in a Pyrex tube. Both the vessel and the tube containing the lamp were immersed in a circulating water bath which kept the temperature at 30°. The salt was photolyzed for 2 hr with 100% of the theoretical amount of nitrogen being evolved as monitored by a gas buret fitted to the side arm of the photolysis vessel. The reaction mixture was worked up as in the above pyrolysis to yield 51 mg (25%) of the naphthylcarbene-diglyme insertion products. It should be noted that while the yield was low, the nmr spectrum of the crude reaction mixture indicated that the diglyme adducts were the major products.

Pyrolysis of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone in Benzene.--To a 3 oz Fischer-Porter Aerosol Compatibility Tube containing 35 ml of benzene was added 0.20 g (0.58 mmol) of the sodium salt of 4,5-benzotropone tosylhydrazone. The sealed tube was placed in an oil bath preheated to 120° and allowed to remain for 2.5 hr. The color of the reaction mixture changed from orange to light yellow during the course of the reaction. Upon cooling, the nitrogen evolution was monitored and 81% of the theoretical amount had evolved. The reaction mixture was filtered and the residue was washed with ethyl ether. The total filtrate was concentrated on a rotary evaporator under reduced pressure to give 122 mg (96%) of crude 2-(2,4,6-cycloheptatrien-1-yl)-naphthalene. Recrystallization from abs methyl alcohol yielded 68 mg (54%) of yellow crystals mp 85-86° (sublimation at 90° and 0.1 mm Hg gave white plates with same mp): ir (KBr) 3060, 3020, 1600, 1500, 1280, 1260, 950, 900, 860, 820, 745, 700, 480 cm^{-1}; nmr ($CDCl_3$) τ 2.10-2.70 (m, 7H, naphthyl), 3.26 (broad t, 2H, 4 and 5 cycloheptatrienyl), 3.55-3.90 (complex m, 2H, 3 and 6 cycloheptatrienyl), 4.33-4.70 (m, 2H, 2 and 7 cycloheptatrienyl), 7.10 (m, 1H, methine); mass spectrum 218 (M+).

Anal. Calcd. for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.39; H, 6.48.

The sodium salt of β-naphthaldehyde tosylhydrazone was pyrolyzed and worked up in a manner analogous to the one above to yield 78% 2-(2,4,6-cycloheptatrien-1-yl)naphthalene and 6% of the aldazine.

Photolysis of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone in Benzene.--To the photolysis vessel, previously described in the photolysis of 4,5-benzotropone tosylhydrazone sodium salt in diglyme, containing 60 ml of benzene was added 0.10 g (0.29 mmol) of the sodium salt of 4,5-benzotropone tosylhydrazone. The mixture was stirred and irradiated with a 550 watt Hanovia medium pressure mercury lamp for 30 min at 30°. The nitrogen evolved was 84% of the theoretical amount. The reaction mixture was filtered and the residue was washed with ethyl ether. The total filtrate was concentrated on a rotary evaporator under reduced pressure to yield 37 mg (59%) of 2-(2,4,6-cycloheptatrien-1-yl)naphthalene which had all the properties of the pyrolysis product.

The sodium salt of β-naphthaldehyde was photolyzed in a manner analogous to the above salt to yield 67% of 2-(2,4,6-cycloheptatrien-1-yl)naphthalene.

Preparation of 2-naphthaldazine.--The compound was prepared by the general procedure given in "Organic Synthesis"[41] and it had mp 235-236°. Lit. 231°.[40]

Pyrolysis of the Sodium Salt of β-Naphthaldehyde Tosylhydrazone in Cyclohexene.--To a 3 oz Fischer-Porter Aerosol Compatibility Tube containing 15 ml of distilled cyclohexene was added 0.40 g (1.15 mmol) of the sodium salt of β-naphthaldehyde tosylhydrazone. The sealed tube was placed in an oil bath preheated to 135° and allowed to remain for 70 min while the temperature was raised to 145°. Upon cooling, the

mixture was filtered and the residue was washed with ethyl ether. The total filtrate was concentrated on a rotary evaporator to yield 212 mg of an oil. Analysis by vpc indicated there were three volatile components which were separated by preparative vpc (column A): (cyclohexene-3-yl)-2-naphthylmethane (34%) retention time 30 min, syn-2-(7-norcaryl)naphthalene (26%) retention time 32 min, and anti-2-(7-norcaryl)naphthalene (40%) retention time 38 min. There was about 10% aldazine formed in the reaction but it did not appear in the vpc chromatogram, thus the above data only refer to volatile hydrocarbon products.

(cyclohexene-3-yl)-2-naphthylmethane showed: ir (film) 3050, 3020, 2920, 2850, 1600, 1500, 1445, 855, 820, 750 cm^{-1}; nmr ($CDCl_3$) τ 2.00-2.90 (m, 7H, naphthyl), 4.40 (s, 2H, vinyl), 7.35 (s, 2H, methylene), 7.80-9.20 (m, 7H, cyclohexyl); mass spectrum 222 (M+).

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.64; H, 8.20.

syn-2-(7-norcaryl)naphthalene showed: mp 68-70°; ir (melt) 3050, 3000, 2930, 2860, 1600, 1500, 1445, 830, 750, 725 cm^{-1}; nmr ($CDCl_3$) τ 2.00-2.80 (m, 7H, naphthyl), 6.60-9.50 (m, 11H, norcaryl); mass spectrum 222 (M+).

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.83; H, 8.20.

anti-2-(7-norcaryl)naphthalene showed: ir (film) 3050, 3005, 2925, 2850, 1625, 1598, 1505, 1442, 809, 778, 740 cm^{-1}; nmr ($CDCl_3$) τ 2.20-3.10 (m, 7H, naphthyl), 7.90-9.30 (m, 11H, norcaryl); mass spectrum 222 (M+).

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.56; H, 8.09.

Pyrolysis of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone in Cyclohexene at 83°.--Into a 50 ml three-neck, round-bottom flask fitted with a thermometer, condenser with a drying tube, and a solid-addition funnel, was placed 25 ml of distilled cyclohexene. The cyclohexene was heated to reflux and 0.10g (0.29 mmol) of the sodium salt of 4,5-benzotropone tosylhydrazone was added by means of the solid-addition funnel. The mixture was heated at reflux for 4 hr and then stopped even though the reaction was incomplete as indicated by the presence of an orange color in the reaction flask. The reaction mixture was filtered and the residue was washed with ethyl ether. The total filtrate was concentrated on a rotary evaporator under reduced pressure. The remaining oil was subjected to vpc analysis (column A) which indicated five volatile components. The ratio of products was two unknown products (66%), the naphthylcarbene-cyclohexene insertion product (7%), syn-norcarane (12%), and anti-norcarane (15%). While neither of the unknown products has been completely characterized, one appears to be the adduct that would result from the addition of benzocycloheptatrienylidene to cyclohexene. The compound showed ir (film) 3010, 2920, 2580, 1585, 1480, 1440, 795, 745, 700 cm^{-1}; nmr ($CDCl_3$) τ 2.75 (d, 4H), 3.25 (d, 1H), 3.60 (d,1H), 4.50 (d, 1H), 4.66 (d, 1H), 8.70 (broad m, 10H); mass spectrum 222 (M+);

uv (95% C_2H_5OH) 240 mμ (log ε = 4.2), 265 (3.5).

Anal. No satisfactory analysis was obtained (probably due to insufficient sample size).

Pyrolysis of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone in Cyclohexene at 140°.--Into a 3 oz Fischer-Porter Aerosol Compatibility Tube containing 15 ml of distilled cyclohexene was introduced 0.40 g (1.15 mmol) of the sodium salt of 4,5-benzotropone tosylhydrazone. The tube was immersed in an oil bath preheated to 135° and allowed to remain for 70 min while the temperature was increased to 145°. The mixture was allowed to cool and was filtered. The residue was washed with ethyl ether and the total filtrate concentrated on a rotary evaporator under reduced pressure to yield 150 mg (58%) of products. Analysis by vpc (column A) indicated the same five products as the 83° pyrolysis: the two "unknown" products, the insertion product, the syn-norcarane, and the anti-norcarane. The amount of unrearranged-carbene products relative to the naphthyl products was approximately the same as in the 83° pyrolysis.

Pyrolysis of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone in Cyclohexene--Diglyme at 82°.--Into a 3 oz Fischer-Porter Aerosol Compatibility Tube containing 17.5 g (0.13 mol) of dry diglyme and 4.95 g (0.06 mol) of distilled cyclohexene was introduced 0.10 g (0.29 mmol) of the sodium salt of 4,5-benzotropone tosylhydrazone. The sealed tube was placed in an oil bath preheated to 82° and allowed to

stir for 11 hr. The reaction mixture was allowed to cool and poured into water (100 ml), extracted with pentane (three 35 ml portions), and the combined pentane extracts washed with water (three 75 ml portions). The pentane solution was dried ($MgSO_4$) and concentrated on a rotary evaporator under reduced pressure to yield 105 mg of products. Analysis of volatile hydrocarbon products by vpc (column A) indicated the "unknown" products, the insertion product, the syn-norcarane, and the anti-norcarane. There were also diglyme insertion products amounting to 27% of the total products. Interfering materials prevented accurate analysis of the mixture.

Photolysis of 4,5-Benzotropone Tosylhydrazone Sodium Salt in Cyclohexene.--To the photolysis vessel, previously described in the photolysis of 4,5-benzotropone tosylhydrazone sodium salt in diglyme, containing 60 ml of distilled cyclohexene was added 200 mg (0.58 mmol) of the sodium salt of 4,5-benzotropone tosylhydrazone. The mixture was stirred and irradiated with a 550 watt Hanovia medium pressure mercury lamp for 1.25 hr. The photosylate was filtered, and the filtrate was concentrated on a rotary evaporator at reduced pressure to yield 67 mg of product. Analysis by vpc (column A) of the volatile hydrocarbon products indicated the "unknown" products, a new, additional unknown product, the insertion product, the syn-norcarane, and the anti-norcarane. The amount of unrearranged-carbene products relative to the naphthyl products appeared to be greater than in the pyrolyses.

Pyrolysis of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone in Cyclohexane.--In a 3 oz Fischer-Porter Aerosol Compatibility Tube containing 20 ml of cyclohexane was placed 0.40 g (1.1 mmol) of the sodium salt of 4,5-benzotropone tosylhydrazone. The sealed tube was placed in an oil bath which was preheated to 115° and allowed to remain for 1.25 hr. Nitrogen evolution was 100% of the theoretical amount. The reaction mixture was allowed to cool and then filtered. The residue was washed with ethyl ether and the total filtrate concentrated on a rotary evaporator under reduced pressure. The remaining yellow oil was chromatographed on alumina, eluted with pentane, yielding 131 mg (51%) of (β-naphthyl) cyclohexylmethane. The nmr spectrum of the crude material indicated almost exclusively adduct and cyclohexane. An analytical sample of the compound was purified by preparative vpc (column A at 222°) retention time 32 min and had the following properties: ir (film) 3042, 3010, 2920, 2845, 1601, 1445, 815, 795 cm^{-1}; nmr ($CDCl_3$) τ 2.10-2.90 (m, 7H, naphthyl), 7.35 (d, 2H, J=7, benzylic), 8.10-9.20 (m, 11H, cyclohexyl); mass spectrum 224 (M+), 141 ($C_{11}H_9$), 83 (C_6H_{11}).

Anal. Calcd. for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 90.84; H, 8.94.

Reaction of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone with Dimethyl Fumarate at 105°.--Into a 3 oz Fischer-Porter Aerosol Compatibility Tube containing 20 ml of benzene were placed 0.20 g (0.58 mmol) of the sodium salt of 4,5-benzotropone tosylhydrazone and 83 mg (0.58 mmol) of

dimethyl fumarate (previously washed with saturated aqueous sodium bicarbonate and then recrystallized from chloroform). The sealed tube was placed in an oil bath preheated to 105° and allowed to remain for 5 hr. Upon cooling, the mixture was filtered. The residue was washed with ethyl ether and the total filtrate concentrated on a rotary evaporator under reduced pressure to yield 76 mg (63%) of 2-(2,4,6-cycloheptatrien-1-yl)naphthalene. The nmr spectrum of the crude reaction material indicated the above mentioned adduct and a considerable amount of unreacted dimethyl fumarate. Comparative tlc on silica gel eluted with 50/50 ethyl ether--pentane of the known pyrazoline (vide infra) and this reaction mixture indicated no pyrazoline was present in the latter.

Reaction of the Sodium Salt of β-Naphthaldehyde Tosylhydrazone with Dimethyl Fumarate at 105°.--To a 3 oz Fischer-Porter Aerosol Compatibility Tube containing 20 ml of benzene was added 0.20 g (0.58 mmol) of the sodium salt of β-naphthaldehyde tosylhydrazone and 83 mg (0.58 mmol) of dimethyl fumarate (previously washed with saturated aqueous sodium bicarbonate and recrystallized from chloroform). The sealed tube was placed in an oil bath preheated to 105° and was allowed to remain there for 5 hr. Upon cooling, the reaction mixture was filtered. The residue was washed with ethyl ether and the total filtrate was concentrated on a rotary evaporator yielding 90 mg (50%) of an almost colorless, very viscous oil. The oil was not stable to ordinary distillation conditions and even though column chromatography on silica gel

effected some purification, it was not sufficient to provide a sample which gave a good elemental analysis (e.g. Calcd. N, 8.97; found: N, 8.31). The other physical data were all consistent with the 3,4-dicarbomethoxy-5-naphthyl-2-pyrazoline structure: ir (film) 3440 (N-H), 3050, 2945, 1730 (unconjugated ester carbonyl), 1700 (conjugated ester carbonyl), 1555 (C=N), 1440, 1200, 1015, 855, 815, and 750 cm^{-1}; nmr ($CDCl_3$) τ 2.10-2.60 (m, 7H, naphthyl), 3.24 (broad s, 1H, nitrogen), 4.60 (broad d, 1H, J=9, benzylic), 5.92 (d, 1H, J=9, α-carbomethoxy), 6.18 (s, 3H, conjugated ester methyl), 6.24 (s, 3H, unconjugated ester methyl)*; mass spectrum no (M+), 284 (M - 28); uv (95% C_2H_5OH) 224 mμ (log ε = 4.53), 275 (3.75), 287 (3.79).

Reaction of β-Naphthaldehyde Tosylhydrazone Sodium Salt with Dimethyl Fumarate at 160°.--This decomposition was carried out in the same manner as the low temperature one with the exception that the sealed tube was placed in an oil bath preheated to 105° and allowed to remain for 2 hr while the temperature was raised to 160°. Upon cooling, the mixture was filtered. The filter paper and the residue were washed with ethyl ether and the total filtrate concentrated on a rotary evaporator under reduced pressure to yield 110 mg (67%)

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* In addition there were other resonances which changed in intensity depending upon work up and purification steps and are, therefore, not believed to originate from the pyrazoline.

of crude trans-1,2-dicarbomethoxy-3-(2-naphthyl)cyclopropane. The solid was recrystallized from abs methyl alcohol to yield 35 mg (21%) of pink needles mp 91-93°: ir (CCl_4) 3028, 2975, 1730, 1435, 1300, 1170, and 909 cm^{-1}; nmr ($CDCl_3$) τ 2.00-2.90 (m, 7H, naphthyl), 6.23 (s, 3H, methyl), 6.58 (s, 3H, methyl), 6.70-7.50 (m, 3H, cyclopropane ring); mass spectrum 284 (M+).

Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67; O, 22.51. Found: C, 71.93; H, 5.73; O, 22.34.

Reaction of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone with Dimethyl Fumarate at 160°.--This decomposition was carried out in the same manner as the low temperature one with the exception that the sealed tube was placed in an oil bath preheated to 105° and allowed to remain for 2 hr while the temperature was raised to 160°. Upon cooling, the mixture was filtered. The residue was washed with ethyl ether and the total filtrate concentrated on a rotary evaporator under reduced pressure. The products were not isolated, only cursorily examined by nmr spectroscopy. The materials, 2-(2,4,6-cycloheptatrien-1-yl)naphthalene and 2-(2,4,6-cycloheptatrien-4-yl)naphthalene, were readily identified by their characteristic spectra and determined to be present in a ratio of 1.0:1.6, respectively, as shown by integration.

General Procedure for the Photolysis of Tosylhydrazone Sodium Salts in the 2-Butenes.--The photolyses were carried out in an apparatus which consisted of a Pyrex tube (20 cm x 2.5 cm) with two side arms and equipped with a small mechanical

stirrer. One of the side arms was connected to a Dry Ice condenser with a drying tube and the other to a stopcock. The desired amount of tosylhydrazone salt was introduced into the apparatus which was consequently flushed with dry nitrogen. The apparatus was then placed in a small Dry Ice-acetone bath and the 2-butene condensed into the vessel. The vessel was then mounted vertically alongside, and as close as possible to, a 550 watt Hanovia medium pressure mercury lamp in a Pyrex cooling jacket. Both the apparatus and the lamp system were placed in a large Dewar flask containing methyl alcohol, with the temperature of the entire system being regulated by the cooling jacket of the lamp which in turn was cooled by a Dry Ice-acetone heat exchanger. The mixture was then rapidly stirred and irradiated for the desired amount of time at temperatures in the range of -15 to -30°.

Photolysis of the Sodium Salt of β-Naphthaldehyde Tosylhydrazone in trans-2-Butene.--Into the previously described photolysis apparatus was placed 0.20 g (0.58 mmol) of the sodium salt of β-naphthaldehyde tosylhydrazone and 30 ml of trans-2-butene (C.P. Grade, typical analysis 99.3 mole % trans-2-butene, 0.2 mole % butene, and 0.5 mole % cis-2-butene). The reaction mixture was irradiated for 2.0 hr at temperatures between -15 to -20°. At the end of this time, the butene was allowed to evaporate and the residue was dissolved in ethyl ether, filtered, and concentrated on a rotary evaporator under reduced pressure to yield 88 mg of a

light yellow oil. In addition to a small amount of unknown products, the material contained three products, 1-(2-naphthyl)-trans-2,3-dimethylcyclopropane, and syn- and anti-1-(2-naphthyl)-cis-2,3-dimethylcyclopropane, as shown by vpc analysis. The trans-cyclopropane was analyzed (column A) and purified by prep vpc (column A).

1-(2-naphthyl)-trans-2,3-dimethylcyclopropane showed: ir (film) 3050, 3000, 2940, 2920, 2860, 1628, 1600, 1500, 1450, 1058, 850, 815, 745 cm^{-1}; nmr (CCl_4) τ 2.10-2.95 (multiplet, 7H, naphthyl protons), 8.15 (multiplet, 1H, proton on C-1), 8.35-9.65 (multiplet, 8H, protons on C-2 and C-3 and methyl protons); mass spectrum m/e 196 (M+).

Anal. Calcd. for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.72; H, 8.31.

Photolysis of Benzaldehyde Tosylhydrazone Sodium Salt in trans-2-Butene.--In the described photolysis apparatus was placed 0.40 g (1.35 mmol) of the sodium salt of benzaldehyde tosylhydrazone,[38] then 25 ml of trans-2-butene (C.P. Grade) was condensed into the apparatus. The reaction mixture was irradiated for 2.5 hr at temp between -15° and -20°. At the end of this time, the butene was allowed to evaporate and the residue was dissolved in ethyl ether, filtered, and concentrated on a rotary evaporator under reduced pressure to yield 0.09 g (45%) of crude 1-phenyl-trans-2,3-dimethylcyclopropane. The cyclopropane was purified by preparative vpc (column A). The nmr ($CDCl_3$) τ 2.93 (broad singlet, 5H, phenyl protons),

8.30 (multiplet, 1H, proton on C-1), 8.68-9.36 (multiplet, 8H, protons on C-2 and C-3 and methyl protons) agreed with the data of Closs.[43]

Photolysis of the Sodium Salt of β-Naphthaldehyde Tosylhydrazone in cis-2-Butene.--The photolysis of the sodium salt of β-naphthaldehyde tosylhydrazone in cis-2-butene was carried out in a manner similar to that of trans-2-butene. In this case, 0.29 g (0.84 mmol) of the sodium salt was decomposed in 30 ml cis-2-butene (C.P. Grade, typical analysis 99.5 mole % cis- and 0.5 mole % trans-2-butene) and the photolysis was done over a period of 2.75 hr at a temp between -20° and -30°. There was produced 0.126 g of a light yellow oil. Again the products were analyzed by vpc and the same three products were present (relative yields): 1-(2-naphthyl)-trans-2,3-dimethylcyclopropane (3%), syn- and anti-1-(2-naphthyl)-cis-2,3-dimethylcyclopropane (97%). The syn- and anti-cyclopropanes were purified by preparative vpc (column A).

syn-1-(2-naphthyl)-cis-2,3-dimethylcyclopropane showed: ir (film) 3050, 3000, 2940, 2870, 1630, 1602, 1500, 1385, 1160, 890, 860, 818, 748 cm^{-1}; nmr (CCl_4) τ 2.20-3.00 (multiplet, 7H, naphthyl protons), 7.90 (multiplet, 1H, proton on C-1), 8.50-9.50 (multiplet, 8H, protons on C-2 and C-3 and methyl protons); mass spectrum m/e 196 (M+).

Anal. Calcd. for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.55; H, 8.15.

anti-1-(2-naphthyl)-cis-2,3-dimethylcyclopropane showed: ir (film) 3050, 3000, 2940, 2860, 1628, 1600, 1500, 1082, 850, 815, 782, 745 cm^{-1}; nmr (CCl_4) τ 2.20-3.10 (multiplet, 7H, naphthyl protons), 8.50-9.15 (multiplet, 9H, protons on C-1, 2, and 3 and methyl protons); mass spectrum m/e 196 (M+).

Anal. Calcd. for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.63; H, 8.29.

Pyrolysis of β-Naphthaldehyde Tosylhydrazone Sodium Salt in cis-2-Butene.--In a 0.5 oz reusable Fischer-Porter Carius Tube was placed 0.10 g (0.29 mmol) of the sodium salt of β-naphthaldehyde tosylhydrazone. The tube was fitted with a Dry Ice condenser by means of a rubber stopper, flushed with dry nitrogen, and placed in a Dry Ice-acetone bath. Then 10 ml of trans-2-butene was condensed into the Carius Tube; the condenser was quickly removed and the tube sealed. The tube was then immersed in an oil bath (preheated to 105°) for 1 hr. At the end of this time the tube was allowed to cool to room temperature and then cooled further in a Dry Ice-acetone bath. The tube was opened, the bath removed, and the butene allowed to evaporate. The residue was dissolved in ethyl ether, concentrated on a rotary evaporator at reduced pressure, and analyzed by vpc (column C) to yield the following data (relative yields): 1-(2-naphthyl)-trans-2,3-dimethylcyclopropane (~10%),* and syn- and anti-1-(2-naphthyl)-cis-2,3-dimethylcyclopropane (~90%).

* A large amount of interfering material makes this data only approximate.

Photolysis of 4,5-Benzotropone Tosylhydrazone Sodium Salt in cis-2-Butene.--The photolysis of the sodium salt of 4,5-benzotropone tosylhydrazone was effected using 0.29 g (0.84 mmol) of the salt in 30 ml of cis-2-butene (C.P. Grade) and by irradiating for 2.3 hr at -25°. Work up yielded 0.061 g of product and vpc analysis (column C) gave the following data: 1-(2-naphthyl)-trans-2,3-dimethylcyclopropane was a minor product (4%); the major products were syn-1-(2-naphthyl)-cis-2,3-dimethylcyclopropane and anti-1-(2-naphthyl)-cis-2,3-dimethylcyclopropane (96%).

Photolysis of 4,5-Benzotropone Tosylhydrazone Sodium Salt in trans-2-Butene.--The photolysis of the sodium salt of 4,5-benzotropone tosylhydrazone was effected as previously described using 0.20 g (0.58 mmol) of the salt in 30 ml of trans-2-butene (C.P. Grade) and by irradiating for 2.3 hr at -25°. Work up yielded 0.046 g of a yellow oil. Vpc analysis (column C) gave the following data: 1-(2-naphthyl)-trans-2,3-dimethylcyclopropane was the major product along with a small amount of the epimeric 1-(2-naphthyl)-cis-2,3-dimethylcyclopropanes.

Pyrolysis of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone in cis-2-Butene.--In a 0.5 oz reusable Fischer-Porter Carius Tube was placed 0.10 g (0.29 mmol) of the sodium salt of 4,5-benzotropone tosylhydrazone. The tube was fitted with a Dry Ice condenser by means of a rubber stopper, flushed with dry nitrogen, and placed in a Dry Ice-acetone

bath. Then, 10 ml of cis-2-butene (research grade) was condensed into the Carius Tube; the condenser was quickly removed and the tube sealed. The tube was allowed to warm to room temperature and then immersed in an oil bath (preheated to 105°) for 3.5 hr. At the end of this time the tube was allowed to cool to room temperature and then cooled further in a Dry Ice-acetone bath. The tube was opened, the bath removed, and the butene allowed to evaporate. The residue was dissolved in ethyl ether, concentrated on a rotary evaporator under reduced pressure to yield 7 mg of a yellow oil which was analyzed by vpc (column C). The reaction material contained the syn- and anti-1-(2-naphthyl)-cis-2,3-dimethylcyclopropanes (93%), 1-(2-naphthyl)-trans-2,3-dimethylcyclopropane (7%), and some extraneous material. In all cases following the percentages given in parentheses do not imply total percent yield but relative yields of the cis- and trans-cyclopropanes and were done on column C unless otherwise stated.

Pyrolysis of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone in cis-2-Butene and Benzene.--The reaction was carried out as in the above experiment except that 0.08 g (0.23 mmol) of the sodium salt, 7.0 ml (79 mmol) of benzene, and 2.5 ml (28 mmol) of research grade cis-2-butene were heated at 105° for 3 hr. The work up was the same yielding 10 mg of a yellow oil which contained the cyclopropanes in the following relative yield: syn- and anti-1-(2-naphthyl)-cis-2,3-dimethylcyclopropanes (94%) and 1-(2-naphthyl)-trans-

2,3-dimethylcyclopropane (6%). The 2-naphthylcarbene-benzene adduct was also produced as evidenced by vpc.

Pyrolysis of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone in cis-2-Butene and Perfluorocyclobutane.--Again, the reaction was carried out in a manner analogous to that of the cis-2-butene reaction. In this series two reactions were carried out: the first with cis-2-butene and perfluorocyclobutane in a 1:2 molar ratio, respectively, and the second with a 1:6 molar ratio, respectively.

In the first reaction, 0.10 g (0.29 mmol) of the sodium salt of benzotropone tosylhydrazone, 8.0 ml (60 mmol) of perfluorocyclobutane, and 2.5 ml (30 mmol) of research grade cis-2-butene were heated at 105° for 5 hr. The work up yielded 7.5 mg of a yellow oil which, when analyzed by vpc, was shown to contain the syn- and anti-1-(2-naphthyl)-cis-2,3-dimethylcyclopropanes (94%) and 1-(2-naphthyl)-trans-2,3-dimethylcyclopropane (6%).

In the second case, 0.10 g (0.29 mmol) of the sodium salt of benzotropone tosylhydrazone, 9.0 ml (67 mmol) of perfluorocyclobutane, and 1.0 ml (11 mmol) of research grade cis-2-butene were heated at 108° for 4 hr. The work up yielded 7.0 mg of a yellow oil which gave the same cis to trans cyclopropane ratio as the first experiment (namely, cis 94% and trans 6%).

Pyrolysis of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone in cis-2-Butene and Oxygen.--This reaction, too, was carried out like the cis-2-butene reaction with the following exceptions: 0.10 g (0.29 mmol) of the sodium salt of benzotropone tosylhydrazone and 12 ml of research grade cis-2-butene were placed in the Carius Tube and then oxygen was bubbled through the mixture for 1 hr. The reaction mixture was heated at 108° for 3.6 hr and the work up yielded 21 mg of a yellow oil which contained the two epimeric cis-cyclopropanes (96%) and the trans-cyclopropane (4%).

A control experiment, done exactly the same as the above experiment only bubbling nitrogen through the mixture, gave the typical 94% cis- material and 6% trans-.

Pyrolysis of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone in cis-2-Butene and trans,trans-2,4-hexadiene.--Again, the reaction was carried out in a manner analogous to that of the cis-2-butene reaction. In this series two separate reactions were carried out: the first with cis-2-butene and trans,trans-2,4-hexadiene in a 1.0:1.5 molar ratio, respectively, and the second with a 1.0:2.1 molar ratio, respectively.

In the first reaction, 0.09 g (0.26 mmol) of the sodium salt of benzotropone tosylhydrazone, 7.0 ml (60 mmol) of trans,trans-2,4-hexadiene, and 3.6 ml (40 mmol) of research grade cis-2-butene were heated at 105° for 4.5 hr. Work up yielded 24 mg of product (again, a yellow oil) which had the cis-cyclopropanes produced in 99% yield relative to the trans-

cyclopropane in 1%. However, what is assumed to be the products from the diene account for ca. 90% of the total products.

In the second case, 0.10 g (0.29 mmol) of the sodium salt of benzotropone tosylhydrazone, 7.3 ml (63 mmol) of trans,trans-2,4-hexadiene, and 2.7 ml (30 mmol) of research grade cis-2-butene were heated at 105° for 5 hr. Work up yielded 18 mg of a yellow oil which proved to be almost exclusively the assumed diene products (there was too little of the butene adducts to provide reliable results).

Sensitized Photolysis of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone in Benzene.--In the photolysis vessel, described previously, was placed 1.0 g (5.1 mmol) xanthen-9-one, 0.10 g (0.29 mmol) of the sodium salt of benzotropone tosylhydrazone, and 40 ml of benzene. The stirred mixture was photolyzed at 30° for 1 hr. The solvent was evaporated and the residue was chromatographed on grade III Woelm basic alumina. There were no hydrocarbon products isolated from the reaction mixture.

Thermal Stability of the syn- and anti-1-(2-naphthyl)-cis-2,3-dimethylcyclopropanes.--A sample of the cis-cyclopropanes was preparatively chromatographed (column A at 230°) and then analyzed for any isomerization during chromatography. There was no trace of trans-cyclopropane as evidenced by vpc analysis (column B).

Stability of cis-2-Butene under Reaction Conditions.--As in a typical run, 0.10 g (0.29 mmol) of the sodium salt of benzotropone tosylhydrazone and 9.0 ml cis-2-butene (research grade) were heated in a Carius Tube at 105° for 4.25 hr. Analysis of the cis-2-butene (column C) after the usual reaction period indicated that less than 1 percent isomerization had occurred during the reaction.

2-Methyl-4,5-Benzotropone.--The ketone was prepared by the method of Heilbronner and had a mp 68-69°. Lit. 70°.[52]

2-Methyl-4,5-Benzotropone Tosylhydrazone.--In a typical run, 2.00 g (0.012 mol) of 2-methyl-4,5-benzotropone, 2.18 g (0.012 mol) of p-toluenesulfonylhydrazide, and 5 drops of concd sulfuric acid were placed in 40 ml of abs ethyl alcohol and heated at reflux for 1 hr. Upon cooling, 2-methyl-4,5-benzotropone tosylhydrazone precipitated from solution and was isolated by filtration. Recrystallization from abs ethyl alcohol yielded 2.4 g (60%) of the product as yellow-gold plates mp 182-184°: ir (KBr) 3180, 1630, 1590, 1555, 1420, 1385, 1330, 1165, 1022, 915, 805, 760, 680, and 580 cm^{-1}; nmr ($CDCl_3$) τ 2.00-3.00 (A_2B_2, 4H, J=8, aromatic), 2.78 (s, 4H, benzo), 3.05-3.70 (m, 3H, cycloheptatrienyl), 7.62 (s, 3H, p-methyl), 7.88 (d, 3H, cycloheptatrienyl methyl); mass spectrum 339 (M+).

Anal. Calcd. for $C_{19}H_{18}N_2O_2S$: C, 67.43; H, 5.36; N, 8.28. Found: C, 67.39; H, 5.33; N, 8.40.

Pyrolysis of the Sodium Salt of 2-Methyl-4,5-Benzotropone Tosylhydrazone in Benzene.--To a Fischer-Porter Aerosol Compatibility Tube containing 35 ml of benzene was added 216 mg (0.60 mmol) of the sodium salt of 2-methyl-4,5-benzotropone tosylhydrazone. The sealed tube was placed in an oil bath preheated to 130° for 20 min. By the end of this time the yellow mixture had changed to a very light yellow-green one. The mixture was allowed to cool and was filtered. The residue was washed with ethyl ether and the total filtrate concentrated on a rotary evaporator under reduced pressure to yield 80 mg of products. Analysis of the product mixture by nmr indicated the presence of 2-vinylnaphthalene and 2-(2,4,6-cycloheptatrien-1-yl)-3-methylnaphthalene (comparisons were made using commercially available 2-vinylnaphthalene from Aldrich Chemical Co. and 2-(2,4,6-cycloheptatrien-1-yl)-3-methylnaphthalene from the pyrolysis of the sodium salt of the tosylhydrazone of 3-methyl-2-naphthaldehyde in benzene). Analysis by vpc (column B) indicated three products in the reaction mixture (the known ones were established by comparison with known samples): 1) retention time 1 min, 2-vinylnaphthalene (72%); 2) retention time 10 min, unknown compound (6%); 3) retention time 14 min, 2-(2,4,6-cycloheptatrien-1-yl)-3-methylnaphthalene (22%). Products 1 and 3 were isolated in 44% and 20% overall yield, respectively. 2-(2,4,6-cycloheptatrien-1-yl)-3-methylnaphthalene (sublimed at 90° and 0.1 mm Hg) had the following properties: mp 65-68°; ir (KBr) 3055, 3010, 1600, 1500, 1440, 1220, 1010, 890, 745, 700, and

480 cm^{-1}; nmr ($CDCl_3$) τ 2.00-2.90 (m, 6H, naphthyl), 3.25 (broad t, 2H, 4 and 5 cycloheptatrienyl), 3.50-3.90 (complex pattern, 2H, 3 and 6 cycloheptatrienyl), 4.35-4.76 (complex pattern, 2H, 2 and 7 cycloheptatrienyl), 6.95 (broad t, 1H, methine), 7.65 (s, 3H, methyl); mass spectrum 232 (M+).

Anal. Calcd. for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.85; H, 7.00.

The sodium salt of 3-methyl-2-naphthaldehyde tosylhydrazone was pyrolyzed in the same manner as the above salt except that 40 ml of benzene was used and the temperature was 145°. The products were aldazine (42%) and 2-(2,4,6-cycloheptatrien-1-yl)-3-methylnaphthalene (39%).

2,3-Benzotropone.--2,3-Benzotropone was prepared by the method of Collington and Jones,[53] and the ir spectrum of the product was in complete agreement with that reported in the literature.

2,3-Benzotropone Tosylhydrazone.--To 1.0 g (0.6 mol) of 2,3-benzotropone in 10 ml of 95% ethyl alcohol was added 1.1 g (0.6 mol) of p-toluenesulfonylhydrazide in 25 ml of 95% ethyl alcohol and one drop of acetic acid. The solution was heated at reflux for 75 min, and then the reaction mixture was allowed to cool. The solvent was removed on a rotary evaporator under reduced pressure and the resinous residue was chromatographed on silica gel eluting with methylene chloride. The thus purified tosylhydrazone, still a viscous resin, was obtained 54% yield and had the following properties:

ir (film) 3210, 1582, 1400, 1385, 1340, 1320, 1160, 1080, 1020, 810, 800, 760, 700, 680, 655 cm^{-1}; nmr ($CDCl_3$) τ 1.60 (broad s, 1H, proton on nitrogen), 2.00-4.00 (multiplet, 12H, protons on benzo ring, cycloheptatriene ring, and the aromatic toluyl protons whose A_2B_2 quarter could be picked out of the multiplet, 7.70 (s, 3H, methyl).

The tosylhydrazone was never obtained in a state of purity which gave a good analysis (e.g. Calcd. C, 65.38; H, 5.16. Found: C, 65.10; H, 5.84). Mass spectrum had no parent peak, (none of any significance above m/e 156 even at 10 eV) 156 (100), 141 (9), 91 (17), 64 (28).

The resinous tosylhydrazone was converted to its sodium salt cleanly by the outlined procedure (this was the only water-sensitive salt made).

Pyrolysis of the Sodium Salt of 2,3-Benzotropone Tosylhydrazone in Benzene.--In a 3 oz Fischer-Porter Aerosol Compatibility Tube containing 35 ml of benzene (deoxygenated by bubbling in nitrogen for several min) was placed 0.28 g (0.81 mmol) of the sodium salt of 2,3-benzotropone tosylhydrazone. The tube was then placed in an oil bath which was preheated to 120° and allowed to remain there for 35 min. The solution was allowed to cool, filtered, and concentrated to a yellow oil on a rotary evaporator under reduced pressure. Chromatography of the residue on activity grade III basic Woelm alumina yielded 0.045 g (26%) of a colorless oil which was identified as 1-(2,4,6-cycloheptatrien-1-yl)naphthalene.

The properties of the compound are as follows: ir (film) 3050, 3020, 1600, 1510, 1395, 800, 780, 745, 705 cm^{-1}; nmr ($CDCl_3$) τ 2.20 (multiplet, 3H, α-protons of naphthyl system), 2.55 (multiplet, 4H, β-protons of naphthyl system), 3.30 (triplet, 2H, J=3 Hz, 4 and 5 protons on cycloheptatriene), 3.70 (multiplet, 2H, 3 and 6 protons on cycloheptatriene), 4.50 (quartet, 2H, J=5.5 Hz, 2 and 7 protons on cycloheptatriene), and 6.60 (multiplet, 1H, 7 proton on cycloheptatriene); mass spectrum m/e 218 (M^+), 127 ($C_{10}H_7$), 91 (C_7H_7).

Anal. Calcd. for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.32; H, 6.61.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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